# **EUROPEAN PATENT SPECIFICATION**

- (45) Date of publication and mention of the grant of the patent:

  03.04.2002 Bulletin 2002/14
- (21) Application number: 96913945.0
- (22) Date of filing: 06.05.1996

(51) Int Cl.7: H01M 4/38

(11)

- (86) International application number: **PCT/US96/06369**
- (87) International publication number: WO 96/36083 (14.11.1996 Gazette 1996/50)
- (54) ELECTROCHEMICAL HYDROGEN STORAGE ALLOYS AND BATTERIES CONTAINING HETEROGENEOUS POWDER PARTICLES

ELEKTROCHEMISCHE WASSERSTOFFSPEICHERLEGIERUNGEN UND BATTERIEN MIT HETEROGENEN PULVERTEILCHEN

ALLIAGES DE STOCKAGE D'HYDROGENE ELECTROCHIMIQUE ET PILES CONTENANT DES PARTICULES DE POUDRE HETEROGENES

- (84) Designated Contracting States:

  AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC

  NL PT SE
- (30) Priority: 08.05.1995 US 436674
- (43) Date of publication of application: 04.03.1998 Bulletin 1998/10
- (73) Proprietor: OVONIC BATTERY COMPANY, INC. Troy, MI 48084 (US)
- (72) Inventors:
  - OVSHINSKY, Stanford, R. Bloomfield Hills, MI 48013 (US)
  - FETCENKO, Michael, A.
     Rochester Hills, MI 48063 (US)
  - CHAO, Benjamin Troy, MI 48084 (US)
  - REICHMAN, Benjamin
     West Bloomfield, MI 48323 (US)
  - YOUNG, Kwo Troy, MI 48098 (US)

- (74) Representative: Kügele, Bernhard et al Novagraaf SA
   25, Avenue du Pailly
   1220 Les Avanchets - Geneva (CH)
- (56) References cited:

JP-A- 61 051 760	JP-A- 61 199 045
US-A- 4 451 445	US-A- 4 582 117
US-A- 4 589 919	US-A- 4 623 597
US-A- 4 789 022	US-A- 4 818 567
US-A- 5 198 207	US-A- 5 376 330
US-A- 5 407 761	US-A- 5 451 474

- PATENT ABSTRACTS OF JAPAN vol. 013, no. 379 (C-628), 22 August 1989 & JP 01 129936 A (SANYO ELECTRIC CO LTD), 23 May 1989,
- PATENT ABSTRACTS OF JAPAN vol. 016, no. 459 (E-1268), 24 September 1992 & JP 04 162355 A (MATSUSHITA ELECTRIC IND CO LTD), 5 June 1992.

P 0 826 249 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

#### Description

10

15

20

25

30

35

40

45

50

55

## Field of the Invention

[0001] The present invention relates to electrochemical hydrogen storage alloys and rechargeable electrochemical cells using heterogeneous alloys.

[0002] More particularly, the invention relates to nickel metal hydride (Ni-MH) rechargeable cells and batteries having negative electrodes formed of heterogeneous alloys. Such alloys are formed from a heterogeneous combination of MgNi based electrochemical hydrogen storage alloys and other types of "Ovonic" (as defined hereinafter) hydrogen storage alloy materials. The heterogeneous formulation can take the form of encapsulation and/or heterogeneous mixing of different alloys to provide enhanced electrochemical performance characteristics. In addition to lower cost, cells that incorporate the alloys of the invention have performance characteristics that are as good as or better than known rechargeable cells using hydrogen storage alloys such as cycle life, charge retention, low temperature, energy density, and especially dramatic increases in electrochemical storage capacity. Another embodiment of the invention focusses on the particular fabrication and characterization of the chemically and structurally modified MgNi alloys to provide remarkable improvements in electrochemical performance in particular hydrogen storage capacity.

## **Background of the Invention**

[0003] In rechargeable alkaline cells, weight and portability are important considerations. It is also advantageous for rechargeable alkaline cells to have long operating lives without the necessity of periodic maintenance. Rechargeable alkaline cells are used in numerous consumer devices such as portable computer, video cameras, and cellular phones. They are often configured into a sealed power pack that is designed as an integral part of a specific device. Rechargeable alkaline cells can also be configured as larger cells that can be used, for example, in industrial, aerospace, and electric vehicle applications.

[0004] For more than three decades, virtually every battery manufacturer in the world studied the NiMH battery technology, but no commercial battery of this kind existed until after the publication of U.S. Patent No. 4,623,597 to Sapru, Reger, Reichman, and Ovshinsky which disclosed Ovshinsky's basic and fundamentally new principles of battery material design. Stanford R. Ovshinsky was responsible for inventing new and fundamentally different electrochemical electrode materials. As predicted by Ovshinsky, reliance on simple, relatively pure compounds was a major shortcoming of the prior art. Relatively pure crystalline compounds were shown to have a low density of hydrogen storage sites, and the type of active sites available occurred accidently and were not designed into the bulk of the material. Thus, the efficiency of the storage of hydrogen and the subsequent release of hydrogen to form water was determined to be poor. By applying his fundamental principles of disorder to electrochemical hydrogen storage, Ovshinsky drastically departed from conventional scientific thinking and created a disordered material having an ordered local environment where the entire bulk of the material was provided with catalytically active hydrogen storage sites as well as other sites which provided the required thermodynamic absorption and release necessary for electrochemical activity.

[0005] Short-range, or local, order is elaborated on in U.S. Patent No. 4,520,039 to Ovshinsky, entitled Compositionally Varied Materials and Method for Synthesizing the Materials, the contents of which are incorporated by reference. This patent disclosed that disordered materials do not require any periodic local order and how spatial and orientational placement of similar or dissimilar atoms or groups of atoms is possible with such increased precision and control of the local configurations that it is possible to produce qualitatively new phenomena. In addition, this patent discusses that the atoms used need not be restricted to "d band" or "f band" atoms, but can be any atom in which the controlled aspects of the interaction with the local environment and/or orbital overlap plays a significant role physically, electronically, or chemically so as to affect physical properties and hence the functions of the materials. The elements of these materials offer a variety of bonding possibilities due to the multidirectionality of d-orbitals. The multidirectionality ("porcupine effect") of d-orbitals provides for a tremendous increase in density and hence active storage sites. These techniques result in means of synthesizing new materials which are disordered in several different senses simultaneously. [0006] Ovshinsky had previously shown that the number of surface sites could be significantly increased by making an amorphous film in which the bulk thereof resembled the surface of the desired relatively pure materials. Ovshinsky also utilized multiple elements to provide additional bonding and local environmental order which allowed the material to attain the required electrochemical characteristics. As Ovshinsky explained in Principles and Applications of Amorphicity, Structural Change, and Optical Information Encoding, 42 Journal De Physique at C4-1096 (Octobre 1981):

Amorphicity is a generic term referring to lack of X-ray diffraction evidence of long-range periodicity and is not a sufficient description of a material. To understand amorphous materials, there are several important factors to be considered: the type of chemical bonding, the number of bonds generated by the local order, that is its coordination,

and the influence of the entire local environment, both chemical and geometrical, upon the resulting varied configurations. Amorphicity is not determined by random packing of atoms viewed as hard spheres nor is the amorphous solid merely a host with atoms imbedded at random. Amorphous materials should be viewed as being composed of an interactive matrix whose electronic configurations are generated by free energy forces and they can be specifically defined by the chemical nature and coordination of the constituent atoms. Utilizing multi-orbital elements and various preparation techniques, one can outwit the normal relaxations that reflect equilibrium conditions and, due to the three-dimensional freedom of the amorphous state, make entirely new types of amorphous materials — chemically modified materials....

[0007] Once amorphicity was understood as a means of introducing surface sites in a film, it was possible to produce "disorder" that takes into account the entire spectrum of effects such as porosity, topology, crystallites, characteristics of sites, and distances between sites. Thus, rather than searching for material changes that would yield ordered materials having a maximum number of accidently occurring surface bonding and surface irregularities, Ovshinsky and his team at ECD began constructing "disordered" materials where the desired irregularities were tailor made. See, U. S. Patent No. 4,623,597, the disclosure of which is incorporated by reference.

[0008] The term "disordered", as used herein to refer to electrochemical electrode materials, corresponds to the meaning of the term as used in the literature, such as the following:

A disordered semiconductor can exist in several structural states. This structural factor constitutes a new variable with which the physical properties of the materials can be controlled. Furthermore, structural disorder opens up the possibility to prepare in a metastable state new compositions and mixtures that far exceed the limits of thermodynamic equilibrium. Hence, we note the following as a further distinguishing feature. In many disordered [materials] ... it is possible to control the *short-range order* parameter and thereby achieve drastic changes in the physical properties of these materials, including forcing new coordination numbers for elements....

S. R. Ovshinsky, *The Shape of Disorder*, 32 *Journal of Non-Crystalline Solids* at 22 (1979) (emphasis added). **[0009]** The "short-range order" of these disordered materials are further explained by Ovshinsky in The Chemical Basis *of Amorphicity: Structure* and Function, 26:8-9 *Rev. Roum. Phys.* at 893-903 (1981):

[S]hort-range order is not conserved .... Indeed, when crystalline symmetry is destroyed, it becomes impossible to retain the same short-range order. The reason for this is that the short-range order is controlled by the force fields of the electron orbitals therefore the environment must be fundamentally different in corresponding crystalline and amorphous solids. In other words, it is the interaction of the local chemical bonds with their surrounding environment which determines the electrical, chemical, and physical properties of the material, and these can never be the same in amorphous materials as they are in crystalline materials . . . The orbital relationships that can exist in three-dimensional space in amorphous but not crystalline materials are the basis for new geometries, many of which are inherently anti-crystalline in nature. Distortion of bonds and displacement of atoms can be an adequate reason to cause amorphicity in single component materials. But to sufficiently understand the amorphicity, one must understand the three-dimensional relationships inherent in the amorphous state, for it is they which generate internal topology incompatible with the translational symmetry of the crystalline lattice .... What is important in the amorphous state is the fact that one can make an infinity of materials that do not have any crystalline counterparts, and that even the ones that do are similar primarily in chemical composition. The spatial and energetic relationships of these atoms can be entirely different in the amorphous and crystalline forms, even though their chemical elements can be the same...

[0010] Based on these principles of disordered materials, described above, three families of extremely efficient electrochemical hydrogen storage negative electrode materials were formulated. These families of negative electrode materials, individually and collectively, will be referred to hereinafter as "Ovonic." One of the families is the La-Ni<sub>5</sub>-type negative electrode materials which have recently been heavily modified through the addition of rare earth elements such as Ce, Pr, and Nd and other metals such as Mn, Al, and Co to become disordered multicomponent alloys, i.e., "Ovonic". The second of these families is the Ti-Ni-type negative electrode materials which were introduced and developed by the assignee of the subject invention and have been heavily modified through the addition of transition metals such as Zr and V and other metallic modifier elements such as Mn, Cr, Al, Fe, etc. to be disordered, multicomponent alloys, i.e., "Ovonic." The third of these families are the disordered, multicomponent MgNi-type negative electrode materials described herein.

[0011] Based on the principles expressed in Ovshinsky's '597 Patent, the OvonicTi-V-Zr-Ni type active materials are disclosed in U.S. Patent No. 4,551,400 to Sapru, Fetcenko, et al. ("the '400 Patent'), the disclosure of which is incorporated by reference. This second family of Ovonic materials reversibly form hydrides in order to store hydrogen. All

25

30

35

20

10

15

45

50

40

.

the materials used in the '400 Patent utilize a Ti-V-Ni composition, where at least Ti, V, and Ni are present with at least one or more of Cr, Zr, and Al. The materials of the '400 Patent are generally multiphase polycrystalline materials, which may contain, but are not limited to, one or more phases of Ti-V-Zr-Ni material with C<sub>14</sub> and C<sub>15</sub> type crystal structures. Other Ovonic Ti-V-Zr-Ni alloys are described in commonly assigned U.S. Patent No. 4,728,586 ("the '586 Patent"), titled Enhanced Charge Retention Electrochemical Hydrogen Storage Alloys and an Enhanced Charge Retention Electrochemical Cell, the disclosure of which is incorporated by reference.

[0012] The characteristic surface roughness of the metal electrolyte interface is a result of the disordered nature of the material as disclosed in commonly assigned U.S. Patent No. 4,716,088 to Reichman, Venkatesan, Fetcenko, Jeffries, Stahl, and Bennet, the disclosure of which is incorporated by reference. Since all of the constituent elements, as well as many alloys and phases thereof, are present throughout the metal, they are also represented at the surfaces and at cracks which form in the metal/electrolyte interface. Thus, the characteristic surface roughness is descriptive of the interaction of the physical and chemical properties of the host metals as well as of the alloys and crystallographic phases of the alloys, in an alkaline environment. The microscopic chemical, physical, and crystallographic parameters of the individual phases within the hydrogen storage alloy material are important in determining its macroscopic electrochemical characteristics.

[0013] In addition to the physical nature of its roughened surface, it has been observed that V-Ti-Zr-Ni type alloys tend to reach a steady state surface condition and particle size. This steady state surface condition is characterized by a relatively high concentration of metallic nickel. These observations are consistent with a relatively high rate of removal through precipitation of the oxides of titanium and zirconium from the surface and a much lower rate of nickel solubilization. The resultant surface has a higher concentration of nickel than would be expected from the bulk composition of the negative hydrogen storage electrode. Nickel in the metallic state is electrically conductive and catalytic, imparting these properties to the surface. As a result, the surface of the negative hydrogen storage electrode is more catalytic and conductive than if the surface contained a higher concentration of insulating oxides.

[0014] The surface of the negative electrode, which has a conductive and catalytic component — the metallic nickel — interacts with metal hydride alloys in catalyzing the electrochemical charge and discharge reaction steps, as well as promoting fast gas recombination.

[0015] Despite the exceptional electrochemical performance now provided by Ovonic, highly disordered nickel metal hydride systems (twice the hydrogen storage capacity of NiCd systems), consumers are demanding increasingly greater run times and power requirements from such rechargeable battery systems. No current battery system can meet these ever-increasing demands. Accordingly, there exists a need for an ultra high capacity, long charge retention, high power delivery, long cycle life, reasonably priced rechargeable battery system.

## Summary of the Invention

10

15

20

25

30

35

45

50

**[0016]** One aspect of the present invention is to provide non-uniform heterogeneous powder particles for the negative electrode of electrochemical cells, such powder particles comprising at least two separate and distinct hydrogen storage alloys. These powder particles will include at least two separate and distinct component alloy systems which can be distinguished by their respective microstructure and preferably either be layered or encapsulating.

**[0017]** Another aspect of the present invention is a method of making powder particles for electrochemical hydrogen storage comprising the steps of: forming a first Ovonic alloy component by mixing and melting wherein said alloy has the following composition:  $(Mg_xNi_{1-x})_aM_b$  where, M represents at least one modifier element chosen from the group consisting of Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Mm, Pd, Pt, and Ca; b ranges from 0 to less than 30 atomic percent; a + b = 100 atomic percent of said first component material;  $0.25 \le x \le 0.75$ ; and forming a second component comprising at least one element chosen from the group consisting of: Ti in the amount of 0 to 60 atomic percent; Zr in the amount of 0 to 40 atomic percent; V in the amount of 0 to 60 atomic percent; Ni in the amount of 0 to 57 atomic percent; Cr in the amount of 0 to 56 atomic percent; Cu in the amount of 0 to 56 atomic percent; Co in the amount of 0 to 15 atomic percent; Mn in the amount of 0 to 20 atomic percent; Al in the amount of 0 to 20 atomic percent; Fe in the amount of 0 to 10 atomic percent; Mo in the amount of 0 to 8 atomic percent; La in the amount of 0 to 30 atomic percent; and Mm in the amount of 0 to 30 atomic percent; where the total amount of the at least one modifier element is equal to 100 atomic percent of the second component material; encapsulating said first component with the second component using a method chosen from a group consisting of melt spinning, gas atomization, ultrasonic atomization, centrifugal atomization, planar flow casting, plasma spray, mechanical alloying, chemical vapor deposition, physical vapor deposition, and chemical deposition.

[0018] Preferably, the second component comprises an Ovonic, i.e., disordered multicomponent material comprising the following elements: Ti in the amount of 0.1 to 60 atomic percent; Zr in the amount of 0.1 to 40 atomic percent; V in the amount of 0 to 60 atomic percent; Ni in the amount of 0.1 to 57 atomic percent; Cr in the amount of 0 to 56 atomic percent; Co in the amount of 0 to 15 atomic percent; Mn in the amount of 0 to 20 atomic percent; Al in the amount of 0 to 8 atomic percent; Fe in the amount of 0 to 6 atomic percent; Mo in the amount of 0 to 10 atomic percent; La in the

amount of 0 to 30 atomic percent; and Mm in the amount of 0 to 30 atomic percent; where the total amount of the elements is equal to 100 atomic percent of the second component.

[0019] Another aspect of the present invention is a method of making powder particles where the first component and the second component, as described above, are mechanically mixed.

[0020] Yet another aspect of the present invention is a powder particle active material for a nickel metal hydride negative electrode comprising a composite material formed from at least two members selected from the group consisting of Ovonic LaNis type alloys, Ovonic TiNi type alloys, and Mg based Ovonic alloys. Another aspect of the present invention is powder particles that comprise a first component alloy and a second component where the first component comprises materials having the following composition:  $(Mg_xNi_{1-x})_aM_b$  where, M represents at least one modifier element chosen from the group consisting of Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Mm, Pd, Pt, and Ca; b ranges from 0 to less than 30 atomic percent; and a + b = 100 atomic percent of said first component;  $0.25 \le x \le 0.75$ ; and the second component comprises at least one element chosen from the group consisting of: Ti in the amount of 0 to 60 atomic percent; Zr in the amount of 0 to 40 atomic percent; V in the amount of 0 to 60 atomic percent; Ni in the amount of 0 to 57 atomic percent; Cr in the amount of 0 to 56 atomic percent; Cu in the amount of 0 to 56 atomic percent; Co in the amount of 0 to 15 atomic percent; Mn in the amount of 0 to 20 atomic percent; Al in the amount of 0 to 20 atomic percent; Fe in the amount of 0 to 10 atomic percent; Mo in the amount of 0 to 8 atomic percent; La in the amount of 0 to 30 atomic percent; and Mm in the amount of 0 to 30 atomic percent; where the total amount of said elements is equal to 100 atomic percent of the second component. In one preferred embodiment, these powder particles are blended composites that exhibit a preferential distribution of the second component on their outer surface thereof.

[0021] The present invention also includes electrochemical hydrogen storage cells having a negative electrode formed from the heterogeneous powder particles described, above.

#### **Detailed Description of the Invention**

[0022] As a result of their experience gained from developing metal hydride negative electrode materials, Ovshinsky and his team have discovered a variety of improved materials for battery electrodes formed of non-uniform heterogeneous powder particles. These powder particles comprise at least two separate and distinct hydrogen storage alloys. The chosen hydrogen storage alloy components can be any combination of crystalline single or multiple phase hydrogen storage alloys or Ovonic hydrogen storage alloys.

**[0023]** More specifically, the hydrogen storage components can be any combination of electrochemical hydrogen storage alloys such as those alloys classified as Ovonic, TiVZrNi type alloys, Ovonic LaNi<sub>5</sub> type alloys, or Ovonic MgNi based alloys (such as described in US-A-5,506,069 or US-A-5,616,432 titled ELECTROCHEMICAL HYDROGEN STORAGE ALLOYS AND BATTERIES FABRICATED FROM MG CONTAINING BASE ALLOYS and filed concurrently with the present application. The present application is a continuation-in-part of both of these applications, and the contents of both of these applications are specifically incorporated by reference.

[0024] The present invention describes alloys that are uniquely formulated to take advantage of the outstanding properties of each of the constituent hydrogen storage component alloys and to avoid any detrimental qualities of these alloys.

**[0025]** An aspect of the present invention, discussed briefly in US-A-5,536,591, involves a new model for understanding the surface properties of negative electrode materials. One important consideration in formulating the alloys of the present invention involves that the proper balance of corrosion and passivation characteristics exists. Reaching such a balance begins with viewing metal hydride negative electrode materials as having a continuum of passivation and corrosive properties, such as shown in Table 1, below.

Table 1 PASSIVATION/CORROSION PROPERTIES				
highly passivating /	1	1	/ / / ////////// / / / <operative window=""></operative>	/ / / highly corrosive
La, Mg			Zr, Mn, Cr, Fe, Ti	V, W, Mo

[0026] With this knowledge, it is possible to formulate combinations of elements to produce electrode materials that will consequently have a proper balance of corrosion and passivation characteristics and fall within the "operative

5

55

50

5

10

15

20

25

30

35

40

45

window" for a particular alloy. Ovonic TiNi type alloys have been optimized for such a balance (see, for example U.S. Patent No. 5,238,756 and 5,277,999, discussed above). Similarly, the production of Ovonic LaNi<sub>5</sub> type electrode materials required the introduction of modifiers to contribute corrosive properties and move these generally passivating alloys into the "operative window." (The term "operative window" is used to refer to the range of passivating and corrosion properties of negative electrode materials which provide for commercially acceptable electrochemical performance characteristics such as cycle life, power, etc.) This operative window is unique for every metal hydride alloy.

[0027] Table 2 below lists modifier groups I, II, III and IV that address a number of elemental modifications possible in the MGNi based alloys of the present invention.

2			
I	п	Ш	īV
Ca	V	В	. Cu
Be	Ti	Bi	Th
Y	Zr	In	Si
<u></u>	Cr	Sb	Zn
	Al		Li
	Fe	i	La
	Sn ,		Mm
			F

[0028] In general, when added as modifiers the elements described in Table 2 make the following contributions to the final alloy mixture:

[0029] Group I, Ca, Be, and Y can partially substitute for Mg. For instance, we expect that the substitution of an element like Ca for perhaps a small portion of the Mg will increase chemical disorder without significantly reducing the hydrogen storage capacity.

[0030] Group II elements permit the custom engineering of metal hydrogen bond strength, activation characteristics, and surface oxide characteristics. The choice of which element or elements in the group will have which specific effect is dependent on the other component elements for a particular Ovonic MgNi based alloy. In general, the effect of the Group II elements are closely interrelated. For example, Ovonic MgNi alloys yield significantly enhanced performance and exceptional bulk material capacity, but they still tend to passivate which indicates that further optimization is necessary to bring them more completely into the operative window. The inventors have shown that optimization of these alloys begins by imparting additional corrosion characteristics to the alloy surface. Such a course adjustment with MgNiCoMn alloys is achieved through the addition of corrosive elements such as V and Al. One can think of the addition of V and Al as useful for the course adjustment of corrosion/passivation properties. Fine adjustment in these MgNiCoMn alloys is achieved through the addition of elements such as Cr, Zr, Fe, Sn, Si, and Cu which can be used in combinations

to achieve the correct balance between corrosion and passivation while maintaining good catalysis and metal hydrogen bond strength.

[0031] The elements in Group III, B, Bi, Sb and In are considered glass formers that effect the formation of crystalline lattices. As stated previously, Ovonic MgNiCoMn alloys have an improved tendency to avoid phase segregation during solidification. It may be possible to completely eliminate phase segregation through processing variations such as faster cooling rates and more careful control of ribbon thickness. Another approach is to provide a base alloy that has an improved resistance to phase segregation. The addition of Group III elements may assist in this regard. The introduction of B, for example, into the lattice network will eliminate or reduce the size of the crystal lattice networks of the material.

5

10

15

25

30

35

40

45

50

55

[0032] Finally, the Group IV elements affect metallurgical properties of the base alloy, particularly disorder, density of state, hardness, and ductility. U.S. Patent No. 4,716,088 describes the concept of surface roughness and the desirability of *in situ* surface area formation and particular elements useful for controlling this property. In the Ovonic MgNi based alloys of the present invention, a similar effect (among others) may be achieved by the addition of Group IV elements such as Li, Zn, La, Ce, Pr, Nd, Mm, and F. Mg in the MgNi based alloys is a rather soft inductor metal. The addition of Group IV element(s) imparts a desirable amount of brittleness. In essence, the addition of Group IV element (s) changes the shape of the MgNi based alloy's stress-strain curve or toughness. As a result, when hydrogen is incorporated into the lattice of the alloy during initial charge/discharge cycling, this brittleness results in the formation of a high surface area through the formation of microcracks. This increase in surface area improves the surface catalysis and discharge rate characteristics.

[0033] Previous work by the present inventors have described the modification of Ovonic MgNi based alloy materials to produce distinct hydrogen storage alloys. The present invention builds on this work and describes a new concept of <u>combining</u> at least two separate and distinct hydrogen storage alloys to produce non-uniform heterogeneous powder particles. The strategy of combining distinct hydrogen storage alloys permits the formulation of negative electrode materials having a degree of passivation/corrosion optimization (and thus increases in performance) that is significantly greater than any previously formulated metal hydride negative electrode materials.

[0034] In this discussion of the invention, heterogeneous powder particles may have two or more separate and distinct hydrogen storage alloys. Such heterogeneous powder particles can specifically include three, four, five, six, ... (ad infinitum) separate and distinct alloys.

[0035] The distinct hydrogen storage alloys of the present invention are not limited to any particular kind of hydrogen storage alloys. The present invention is intended to encompass the combination of separate and distinct hydrogen storage alloys that have been variously described as single phase and multiple phase, crystalline, as well as disordered materials. Such alloys have commonly been referred to by a variety of terms such as Ovonic TiNi, type alloys, Ovonic LaNi<sub>5</sub> type alloys, Ovonic MgNi type alloys, etc. Any known type of metal hydride electrochemical material may be used as each of the at least two separate and distinct hydrogen storage alloys that make up the heterogeneous powder particles of the present invention. Preferably, each distinct hydrogen storage alloy can be generally classified as an Ovonic nickel metal hydride as disclosed in U.S. Patent No. 4,623,597. Specific examples of the separate and distinct Ovonic alloys that can comprise the heterogeneous powder particles of the present the invention include the TiNi type alloys described in U.S. Patent Nos. 4,551,400; 4,637,967; 4,728.586; 5,096,667; 5,104,617; 5,135,589; 5,238,756; and 5,277,999; as well as the LaNi<sub>5</sub> type alloys described in U.S. Patent Nos. 3,874,928; 4,214,043; 4,107,395; 4,107,405; 4,112,199; 4,125,688; 4,214,043; 4,216,274; 4,487,817; 4,605,603; 4,696,873; 4,699,856 (all of which are discussed in U.S. Patent No. 5,238,756).

[0036] Preferred heterogeneous powder particles of the invention are also formed from at least one Ovonic MgNi based alloy and at least one other separate and distinct hydrogen storage alloy. An example of an Ovonic MgNi based alloy is the following:

# $(Mg_xNi_{1-x})_aM_b$

where, M represents at least one modifier element chosen from the group consisting of Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Mm, Pd, Pt, and Ca; b ranges from 0 to less than 30 atomic percent; and a + b = 100 atomic percent of the alloy;  $0.25 \le x \le 0.75$ . This alloy is intended to encompass unmodified Mg alloys as well as modified Mg alloys. Such alloys are described in detail in US-A-5,506,069, the contents of which are incorporated by reference. In general, one of the separate and distinct hydrogen storage alloys can comprise at least one element chosen from the group consisting of Ti in the amount of 0 to 60 atomic percent; Zr in the amount of 0 to 40 atomic percent; V in the amount of 0 to 60 atomic percent; Ni in the amount of 0 to 57 atomic percent; Cr in the amount of 0 to 56 atomic percent; Co in the amount of 0 to 15 atomic percent; Mn in the amount of 0 to 20 atomic percent; Al in the amount of 0 to 30 atomic percent; and Mm in the amount of 0 to 8 atomic percent; La in the amount of 0 to 30 atomic percent; and Mm in the amount

of 0 to 30 atomic percent; where the total amount of the components is equal to 100 atomic percent of the alloy. [0037] Such Ovonic hydrogen storage alloys may be one of a variety of known materials such as those described in U.S. Patent No. 4,849,205, GB 1,571,299, EP 0 484 964, U.S. Patent No. 5,131,920, EP 0 450 590 A1, EP 0 468 568 A1, and EP 0 484 964 A1. Specific examples of compositional formulae of disordered hydrogen storage alloys of the present invention are the following: An alloy represented by the formula ZrMn<sub>w</sub>V<sub>x</sub>M<sub>y</sub>Ni<sub>z</sub>, where M is Fe or Co and w, x, y, and z are mole ratios of the respective elements where  $0.4 \le w \le 0.8$ ,  $0.1 \le x \le 0.3$ ,  $0 \le y \le 0.2$ ,  $1.0 \le z \le 1.5$ , and  $2.0 \le w + x + y + z \le 2.4$ . An alloy in which one of the components La or Ni is substituted by a metal M selected from Groups Ia, II, III, IV, and Va of the Periodic Table of the Elements other than lanthanides, in an atomic proportion which is higher than 0.1% and lower than 25%. An alloy having the formula  $TiV_{2-x}Ni_x$ , where x = 0.2 to 0.6. An alloy having the formula  $T_{i_a}Z_{r_b}N_{i_c}Cr_dM_x$ , where M is Al, Si, V, Mn, Fe, Co, Cu, Nb, Ag, or Pd,  $0.1 \le a \le 1.4$ ,  $0.1 \le b \le 1.3$ ,  $0.25 \le c \le 1.95$ ,  $0.1 \le d \le 1.4$ , a + b + c + d = 3, and  $0 \le x \le 0.2$ . An alloy having the formula  $ZrMo_dNi_e$  where d = 0.1to 1.2 and e = 1.1 to 2.5. An alloy having the formula  $T_{1-x}Zr_xMn_{2-y-z}Cr_yV_z$  where  $0.05 \le x \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 1.0$ , and  $0 < z \le 0.4$ ,  $0 < y \le 0.4$ , and  $0 < z \le 0.4$ ,  $0 < y \le 0.4$ , 0 <≤ 0.4. An alloy having the formula LnM<sub>5</sub> where Ln is at least one lanthanide metal and M is at least one metal chosen from the group consisting of Ni and Co. An alloy comprising at least one transition metal forming 40-75% by weight of the alloy chosen from Groups II, IV, and V of the Periodic System, and at least one additional metal, making up the balance of the alloy, alloyed with the at least one transitional metal, this additional metal chosen from the group consisting of Ni, Cu, Ag, Fe, and Cr-Ni steel. An alloy comprising a main texture of Mm -Ni system; and a plurality of compound phases where each compound phase is segregated in the main texture, and wherein the volume of each of the compound phases is less than about 10 μm<sup>3</sup>.

10

15

20

25

30

35

40

45

50

55

[0038] Some specific examples of Ovonic hydrogen storage alloys and disordered hydrogen storage alloys are  $Ti_{0.3}Cr_{0.3}Zr_{0.5}Ni_{0.7}V_{1.2}Cu_{0.1}$ 

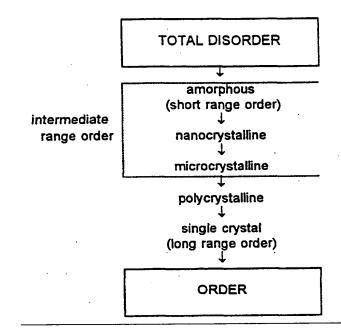
The Most preferred heterogeneous powder particles are formed from at least one Ovonic MgNi based alloy (as described in US-A-5, 506,069 and at least one Ovonic TiNi type or LaNi<sub>5</sub> type hydrogen storage alloy.

[0040] Generally, Ovonic TiNi type hydrogen storage alloys consist of a Base Alloy and modifiers. The preferred formulations of the Base Alloy contain 0.1 to 60 atomic percent Ti, 0.1 to 40 atomic percent Zr, 0 to 60 atomic percent V, 0.1 to 57 atomic percent Ni, and 0 to 56 atomic percent Cr. The most preferred formulations of this Base Alloy contain 0.1 to 60 atomic percent Ti, 0.1 to 40 atomic percent Zr, 0.1 to 60 atomic percent V, 0.1 to 57 atomic percent Ni, and 0 to 56 atomic percent Cr.

[0041] Specific examples of preferred Ovonic TiNi type hydrogen storage alloys for use as at least one component of the heterogeneous powder particles materials are set forth in Table 3, below.

	٦	Table 3	
1.	V <sub>5</sub> Ti <sub>9</sub> Zr <sub>27</sub> Ni <sub>38</sub> Cr <sub>5</sub> Mn <sub>16</sub>	14.	$V_4Ti_9Zr_{27}Ni_{37}Co_5Mn_{15}Fe_3Sn_{0.4}$
2.	V <sub>5</sub> Ti <sub>9</sub> Zr <sub>27</sub> Ni <sub>38</sub> Co <sub>5</sub> Mn <sub>18</sub>	15.	V <sub>3</sub> Ti <sub>9</sub> Zr <sub>28</sub> Ni <sub>37</sub> Co <sub>5</sub> Mn <sub>15</sub> Fe <sub>3</sub> Sn <sub>0.6</sub>
3.	V <sub>5</sub> Ti <sub>9</sub> Zr <sub>26</sub> Ni <sub>38</sub> Co <sub>5</sub> Mn <sub>16</sub> Fe <sub>1</sub>	16.	Ti <sub>10</sub> Zr <sub>28</sub> Ni <sub>36</sub> Co <sub>5</sub> Cr <sub>5</sub> Mn <sub>16</sub>
4.	V <sub>5</sub> Ti <sub>9</sub> Zr <sub>26</sub> Ni <sub>38</sub> Co <sub>5</sub> Mn <sub>15</sub> Fe <sub>2</sub>	17.	Ti <sub>10</sub> Zr <sub>27</sub> Ni <sub>36</sub> Co <sub>5</sub> Cr <sub>4</sub> Mn <sub>13</sub> Fe <sub>5</sub>
5.	V <sub>5</sub> Ti <sub>9</sub> Zr <sub>26</sub> Ni <sub>37</sub> Co <sub>5</sub> Mn <sub>15</sub> Fe <sub>3</sub>	18.	Ti <sub>12</sub> Zr <sub>29</sub> Ni <sub>34</sub> Co <sub>5</sub> Cr <sub>5</sub> Mn <sub>15</sub>
6.	V <sub>5</sub> Ti <sub>9</sub> Zr <sub>26</sub> Ni <sub>36</sub> Co <sub>5</sub> Mn <sub>15</sub> Fe <sub>4</sub>	19.	Ti <sub>13</sub> Zr <sub>30</sub> Ni <sub>34</sub> Co <sub>5</sub> Cr <sub>3</sub> Mn <sub>15</sub>
7.	V <sub>5</sub> Ti <sub>9</sub> Zr <sub>26</sub> Ni <sub>35</sub> Co <sub>5</sub> Mn <sub>15</sub> Fe <sub>5</sub>	20.	Ti <sub>12</sub> Zr <sub>29</sub> Ni <sub>34</sub> Co <sub>7</sub> Cr <sub>1</sub> Mn <sub>15</sub> Fe <sub>2</sub>
8.	V <sub>7</sub> Ti <sub>9</sub> Zr <sub>24</sub> Ni <sub>36</sub> Co <sub>5</sub> Mn <sub>16</sub> Fe <sub>3</sub>	21.	$V_1T_{10}Zr_{28}Ni_{34}Cr_3Co_6Mn_{14}Fe_2$
9.	V <sub>6</sub> Ti <sub>9</sub> Zr <sub>28</sub> Ni <sub>35</sub> Co <sub>5</sub> Mn <sub>15</sub> Fe <sub>2</sub>	22.	V <sub>2</sub> Ti <sub>10</sub> Zr <sub>26</sub> Ni <sub>34</sub> Cr <sub>3</sub> Co <sub>6</sub> Mn <sub>14</sub> Fe <sub>2</sub> Sn <sub>1</sub>
10.	V <sub>4</sub> Ti <sub>10</sub> Zr <sub>29</sub> Ni <sub>35</sub> Co <sub>5</sub> Mn <sub>15</sub> Fe <sub>2</sub>	23.	V <sub>0.2</sub> Ti <sub>10</sub> Zr <sub>28</sub> Ni <sub>36</sub> Co <sub>5</sub> Cr <sub>5</sub> Mn <sub>16</sub>
11.	V <sub>4</sub> Ti <sub>9</sub> Zr <sub>28</sub> Ni <sub>37</sub> Co <sub>5</sub> Mn <sub>15</sub> Fe <sub>2</sub> Sn <sub>0.4</sub>	24.	V <sub>0.2</sub> Ti <sub>12</sub> Zr <sub>29</sub> Ni <sub>34</sub> Co <sub>7</sub> Cr <sub>1</sub> Mn <sub>15</sub> Fe <sub>2</sub>
12.	V <sub>3</sub> Ti <sub>9</sub> Zr <sub>26</sub> Ni <sub>38</sub> Co <sub>5</sub> Mn <sub>15</sub> Fe <sub>2</sub> Sn <sub>0.4</sub>	25.	V <sub>0.5</sub> Ti <sub>10</sub> Zr <sub>26</sub> Ni <sub>34</sub> Co <sub>6</sub> Cr <sub>3</sub> Mn <sub>14</sub> Fe <sub>2</sub> Sn <sub>2</sub>
13.	V <sub>4</sub> Ti <sub>9</sub> Zr <sub>27</sub> Ni <sub>38</sub> Co <sub>5</sub> Mn <sub>15</sub> Fe <sub>2</sub> Sn <sub>0.4</sub>		
1			

The microstructure of the heterogeneous powder particles of the current invention can fall anywhere along the following continuum depending upon the degree of disorder thereof:



[0043] Of course, the microstructure of the heterogeneous powder particles of the present invention can consist of multiple phases of different microstructures such as intermediate range order, as defined in U.S. Paternt Application No. 08/436,673, polycrystalline materials in each of the separate and distinct hydrogen storage alloys respectively. [0044] The arrangement of the at least two separate and distinct hydrogen storage alloys of the present invention can be a composite mixture, a lamellar structure, or an encapsulated particle. The desirability of one of these structures over the other is dependent on which at least two separate and distinct hydrogen storage alloys are chosen as the components of the ultimate heterogeneous powder particles. In most cases, a composite mixture, where the quantities of each separate and distinct hydrogen storage alloy are chosen to produce a heterogeneous powder particle having the required amount of passivation and corrosion, as well as other characteristics, is adequate to produce an alloy exhibiting superior electrochemical performance. In other cases, where one of the at least two separate and distinct hydrogen storage alloys has a characteristic, such as catalysis, that gives improved electrochemical performance if placed in intimate contact with a second of the at least two separate and distinct hydrogen storage alloys having a complimentary performance characteristic, such as hydrogen storage, then a lamellar structure is preferable so as to physically juxtapose the storage/catalysis components in close proximity thereby shortening paths of hydrogen solid state diffusion.

[0045] Finally, alloy characteristics may warrant the encapsulation of one hydrogen storage alloy by the other. This structure is particularly useful when using magnesium based alloys as a component of the heterogeneous particle. Magnesium based alloys have excellent storage capacity, yet simple or unmodified MgNi based alloys have a tendency to passivate in alkaline electrolyte. Encapsulation is one method of effectively protecting Mg from the corrosive alkaline environment inside an electrochemical cell while still providing for the efficient absorption/desorption of hydrogen.

[0046] A preferred encapsulated heterogeneous powder particle uses at least one Ovonic MgNi based alloy encapsulated with at least one Ovonic metal hydride alloy laminating the surface thereof.

[0047] One method for forming the heterogeneous powder particles of the present invention is to form one or all of the at least two separate and distinct hydrogen storage alloys using a conventional melt-hydride-grind processes.

[0048] Another method is to form one or all of the at least two separate and distinct hydrogen storage alloys using rapid solidification. Rapid solidification refers to methods and processes for rapidly quenching a material from the liquid state into the solid state at a quench rate sufficiently high to freeze the positions of the atoms in their atomic arrangements. Typically, the material is ejected in its liquid state into a high quench environment such as onto a chill wheel where it solidifies before complete crystallization can begin. Generally, the rapid solidification processes are to be contrasted to the thin film deposition processes such as sputtering or vacuum deposition which are conducted at low rates of particle transfer or to a substrate to form a thin film. Preferably, the rapid solidification processes commonly referred to as melt spinning, jet casting, multiple jet casting, or planar flow casting are used. Any of these rapid solidification processes can be used regardless of the particular apparatus used or details of the process itself. In addition, It is possible to introduce chemical and structural disorder on an atomic scale by the use of processing methods such as described in Ovshinsky, et al.'s U.S. Patent No. 4,339,255 (the contents of which are incorporated by reference).

This patent describes rapid quenching multiple streams of material (such as a stream of Base Alloy and a stream of modifier elements) where the flow and quench rate of each stream of material are independently controlled. With respect to the present invention, this technique is particularly useful with modifier(s) of very high melting point or with modifier(s) that are quite different from the host MgNi.

[0049] Once the at least two separate and distinct hydrogen storage alloys have been formulated, they may be combined using any fabrication method that effectively permits the retention of their separate and distinct nature. For example, the at least two separate and distinct hydrogen storage alloys may be combined using mechanical alloying, compaction, sintering, or some combination of these methods. It is also foreseeable that the distinct alloys could be combined using some variation of melt spinning or jet casting that would permit the alloys to retain their separate and distinct natures. Mechanical blending or alloying techniques such as ball milling or impact block mixing must be done for a sufficient time to provide electrical connectivity between individual particles. However, these procedures cannot be continued for such a period of time that the separate and distinct nature of the at least two hydrogen storage alloys is destroyed, or that fine powder particle agglomerate together, limiting surface area and catalysis.

### Examples

5

10

15

20

25

50

55

[0050] Thin film materials were prepared in order to rapidly analyze the electrochemical performance characteristics of the combination of separate and distinct alloys of the present invention.

[0051] A series of films with different chemical compositions were deposited using laser ablation. Laser ablation was chosen due to its unique capability to transfer target stoichiometry to a substrate. In other words, such a laser technique reduces the effort necessary to balance the chemical composition of the target such as is required with other deposition techniques like sputtering and co-evaporation.

[0052] The laser ablation depositions were performed in a four target chamber using a 50 watt exciter laser at 248 nm. The primary target first component material was made by hot-pressing a mixed powder of Mg<sub>2</sub>Ni, Ni, and Co with a composition of 52 at.% Mg, 45 at.%Ni, 3 at.% Co. The second target of second component material was made from  $V_{18}$ Ti<sub>15</sub>Zr<sub>18</sub>Ni<sub>29</sub>Cr<sub>5</sub>Co<sub>7</sub>Mn<sub>8</sub> material manufactured by the Ovonic Battery Company as negative electrode material compacted onto a Ni mesh substrate. The deposition parameters for the first component and the second component, respectively, are listed in Table 1.

30	Table 1			
		First Component	Second Component	
	Laser Wavelength	248 nm	248 nm	
	Pulse Width	20 nsec	20 nsec	
35	Pulse Rate	10 Hz	10 Hz	
	Laser Fluence	5 Joule/cm <sup>2</sup>	5 Joule/cm <sup>2</sup>	
	Deposition Rate	1.5 micron/hour	1.5 micron/hour	
40	Deposition Time	2 hour	2 hour	
	Background Gas	Не	He	
	Background Pressure	200 mTorr	200 mTorr	
45	Substrate Temperature	25° C	25° C	
45	Substrate	: Ni foil	Ni foil	

[0053] After the deposition, sample electrochemical cells were prepared using the thin films described in Table 2 as the negative electrode in a oxygen-free flooded cell. The positive electrode was sintered Ni(OH)2. The electrolyte was a 30 wt.% KOH solution. The sample cells were charged using a constant current at a rate of 100 mA/g for 10 hours and discharged at a current of either 100 mA/g or 50 mA/g to 0.9 V with respect to the positive electrode. The measured hydrogen storage capacities for each electrode are listed in Table II. After ten cycles, a significant improvement in capacity was observed. The inventors believe that this increase is due to the presence of the second component Ovonic alloy that encapsulates the Ovonic MgNi based alloy, imparts a significant degree corrosion resistance to the MgNi based alloy and provides an increased number of catalytic sites.

Table 2

5	substrate temp during encapsulant deposition	encapsulant thickness	Capacity (mAh/g)				
			Cycle 1 100 mA/g	Cycle 6 50 mA/g	Cycle 11 50 mA/g	Cycle 16 50 mA/g	Cycle 21 50 mA/g
10	none	none	406	253	206	179	179
	100°C	0.5	0	3	6	12	6
•	250°C	0.5	6	18	51	66	21
15	400°C	0.5	163	157	402	378	390
,,,	400°C	0.5	124	133	326	335	513
	400°C	0.25	136	230	547	441	607
	400°C	0.25	130	133	311	302	420
20	450°C	0.5	109	133	320	290	347
	450°C	0.5	130	145	356	362	465

[0054] In view of the above, it is obvious to those skilled in the art that the present invention identies and encompasses a range of alloy compositions which, when incorporated as a disordered negative electrode in metal hydride cells, results in batteries having improved electrochemical performance characteristics.

#### Claims

30

25

35

45

50

55

Non-uniform heterogeneous composite powder particles for electrochemical uses, where each of said non-uniform
heterogeneous composite powder particles comprises at least two separate and distinct hydrogen storage alloys
blended together and where one of said at least two separate and distinct hydrogen storage alloys is a Mg based
alloy.

The non-uniform heterogeneous composite powder particles of claim 1, wherein said non-uniform heterogeneous
composite powder particles comprise at least two separate and distinct alloy components when distinguished on
the micron level.

- 3. The non-uniform heterogeneous composite powder particles of claim 2, wherein said non-uniform heterogeneous composite powder particles have a lamellar structure.
  - 4. The non-uniform heterogeneous composite powder particles of claim 1, where a first alloy of said at least two separate and distinct hydrogen storage alloys comprises materials having the following composition:

(Mg<sub>x</sub> Ni<sub>1-x</sub>)<sub>a</sub> M<sub>b</sub>

where,

M represents at least one modifier element chosen from the group consisting of Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, and Ca;

b ranges from 0 to less than 30 atomic percent; and

a+b=100 atomic percent of said first alloy;

 $0.25 \le x \le 0.75$ ; and

where a second alloy of said at least two separate and distinct hydrogen storage alloys comprises components chosen from a group consisting of:

Ti in the amount of 0 to 60 atomic percent;

Zr in the amount of 0 to 40 atomic percent; V in the amount of 0 to 60 atomic percent; Ni in the amount of 0 to 57 atomic percent; Cr in the amount of 0 to 56 atomic percent; Cu in the amount of 0 to 56 atomic percent; Co in the amount of 0 to 15 atomic percent; Mn in the amount of 0 to 20 atomic percent; Al in the amount of 0 to 20 atomic percent; Fe in the amount of 0 to 10 atomic percent; Mo in the amount of 0 to 8 atomic percent; La in the amount of 0 to 30 atomic percent; and Mm in the amount of 0 to 30 atomic percent;

where the total amount of said components is equal to 100 atomic percent of said second alloy.

5. Non-uniform heterogeneous composite powder particles for electrochemical uses, said powder particles comprising at least two separate and distinct hydrogen storage alloys where a first alloy of said at least two separate and distinct hydrogen storage alloys comprises materials having the following composition:

(Mg<sub>x</sub> Ni<sub>1-x</sub>)<sub>a</sub> M<sub>b</sub>

where,

5

10

15

20

25

30

35

40

45

M represents at least one modifier element chosen from the group consisting of Ni, CO, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, and Ca;

b ranges from 0 to less than 30, atomic percent; and

a+b=100 atomic percent of said first alloy;

 $0.25 \le x \le 0.75$ ; and,

where a second alloys of said at least two separate and distinct hydrogen storage alloys comprises components chosen from a group consisting of;

Ti in the amount of 0 to 60 atomic percent;

V in the amount of 0 to 60 atomic percent;

Zr in the amount of 0 to 40 atomic percent;

Ni in the amount of 0 to 57 atomic percent;

Cr in the amount of 0 to 56 atomic percent;

Cu in the amount of 0 to 56 atomic percent; Co in the amount of 0 to 15 atomic percent;

Mn in the amount of 0 to 20 atomic percent;

Al in the amount of 0 to 20 atomic percent;

Fe in the amount of 0 to 10 atomic percent;

Mo in the amount of 0 to 8 atomic percent:

La in the amount of 0 to 30 atomic percent; and

Mm in the amount of 0 to 30 atomic percent;

where the total amount of said components is equal to 100 atomic percent of said second alloy; and said second alloy encapsulates said first alloy.

- 6. The non-uniform heterogeneous composite powder particles of claim 5, where said second alloy is present as intimately mixed striations with said first alloy.
  - 7. The non-uniform heterogeneous composite powder of claim 5, where said powder particles comprise blended composite powder particles of said second alloy and said first alloy.
- 55 **8.** The non-uniform heterogeneous composite powder particles of claim 5, where said powder particles exhibit a preferential distribution of said second alloy on their surface.
  - 9. The non-uniform heterogeneous composite powder particles of claim 5, where said second alloy material com-

prises a disordered multicomponent material comprising the following components:

Ti in the amount of 0.1 to 60 atomic percent; Zr in the amount of 0.1 to 25 atomic percent; V in the amount of 0 to 60 atomic percent; Ni in the amount of 0.1 to 57 atomic percent; Cr in the amount of 0.1 to 56 atomic percent; Co in the amount of 0 to 7 atomic percent; Mn in the amount of 4.5 to 8.5 atomic percent; Al in the amount of 0 to 3 atomic percent; Fe in the amount of 0 to 2.5 atomic percent; Mo in the amount of 0 to 5.5 atomic percent; La in the amount of 0 to 30 atomic percent; and Mm in the amount of 0 to 30 atomic percent;

15

20

25

35

40

45

55

10

where the total amount of said components is equal to 100 atomic percent of said second component material.

10. The non-uniform heterogeneous composite powder particles of claim 5, where said second alloy has the following composition:

 $V_{18}Ti_{15}Zr_{18}Ni_{29}Cr_5Co_7Mn_8$ .

11. The non-uniform heterogeneous composite powder particles of claim 5, where said first alloy has the following composition:

(base Alloy)<sub>a</sub> M<sub>b</sub>

30 where,

Base Alloy is an alloy of Mg and Ni in a ratio of from about 1:2 to about 2:1;

M represents at least one modifier element chosen from the group consisting of Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, and Ca; b is greater than 0.5 atomic percent and less than 30 atomic percent; and

a+b=100 atomic percent of said first component material.

12. A method of making non-uniform heterogeneous composite powder particles for electrochemical hydrogen storage comprising:

forming a first component by mixing and melting where said alloy has the following composition:

(Mg<sub>x</sub> Ni<sub>1-x</sub>)<sub>a</sub> M<sub>b</sub>

where

M represents at least one modifier element chosen from the group consisting of Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, and Ca;

b ranges from 0 to less than 30 atomic percent;

a+b=100 atomic percent of said first component material;

 $0.25 \le x \le 0.75$ ; and

forming a second component comprising at least one element chosen from the group consisting of:

Ti in the amount of 0 to 60 atomic percent; Zr in the amount of 0 to 40 atomic percent; V in the amount of 0 to 60 atomic percent; Ni in the amount of 0 to 57 atomic percent; Cr in the amount of 0 to 56 atomic percent; Cu in the amount of 0 to 56 atomic percent; Co in the amount of 0 to 15 atomic percent;

Mn in the amount of 0 to 20 atomic percent; Al in the amount of 0 to 20 atomic percent; Fe in the amount of 0 to 10 atomic percent; Mo in the amount of 0 to 8 atomic percent; La in the amount of 0 to 30 atomic percent; and Mm in the amount of 0 to 30 atomic percent;

where the total amount of said components is equal to 100 atomic percent of said second component material; encapsulating said first component with said second component.

10

5

- 13. The method of making non-uniform heterogeneous composite powder particles for electrochemical hydrogen storage of claim 12, where said encapsulating step is accomplished using a method chosen from a group consisting of melt spinning, gas atomization, ultrasonic atomization, centrifugal atomization, planar flow casting, plasma spray, mechanical alloying, and vapor deposition.
- 15
- 14. The method of making non-uniform heterogeneous composite powder particles for electrochemical hydrogen storage of claim 12, where said second component comprises a disordered multicomponent material comprising the following elements:
- 20

25

30

Ti in the amount of 0.1 to 60 atomic percent; Zr in the amount of 0.1 to 25 atomic percent; V in the amount of 0 to 60 atomic percent; Ni in the amount of 0.1 to 57 atomic percent; Cr in the amount of 0.1 to 56 atomic percent: Co in the amount of 0 to 7 atomic percent; Mn in the amount of 4.5 to 8.5 atomic percent; Al in the amount of 0. to 3 atomic percent; Fe in the amount of 0 to 2.5 atomic percent; Mo in the amount of 0 to 6.5 atomic percent; La in the amount of 0 to 30 atomic percent; and

Mm in the amount of 0 to 30 atomic percent;

where the total amount of said elements is equal to 100 atomic percent of said second component.

35

15. The method of making non-uniform heterogeneous composite powder particles for electrochemical hydrogen storage of claim 12, where said second component comprises an alloy of the following composition:

V<sub>18</sub>Ti<sub>15</sub>Zr<sub>18</sub>Ni<sub>29</sub>Cr<sub>5</sub>Co<sub>7</sub>Mn<sub>8</sub>.

40

16. The method of making non-uniform heterogeneous composite powder particles for electrochemical hydrogen storage of claim 12, where said first component comprises an alloy of the following composition:

(Base Alloy), Mb

45

50

where,

Base Alloy is an alloy of Mg and Ni in a ratio of from about 1:2 to about 2:1;

M represents at least one modifier element chosen from the group consisting of Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li Cd, Na, Pb, La, Ce, Pr, Nd, Mm, and Ca; b is greater than 0.5 atomic percent, and less than 30 atomic percent; and

a+b=100 atomic percent of said first component.

55

17. A method of making non-uniform heterogeneous composite powder particles for electrochemical hydrogen storage comprising the steps of:

forming a first component having the following composition:

# $(Mg_xNi_{1-x})_aM_b$

where.

10

15

20

25

30

M represents at least one modifier element chosen from the group consisting of Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, and Ca; b ranges from 0 to less than 30 atomic percent;

a + b = 100 atomic percent of said first component material;

 $0.25 \le x \le 0.75$ ;

forming a second component that is a disordered multicomponent material comprising the following elements:

Ti in the amount of 0.1 to 60 atomic percent; Zr in the amount of 0.1 to 25 atomic percent; V in the amount of 0 to 60 atomic percent; Ni in the amount of 0.1 to 57 atomic percent; Cr in the amount of 0.1 to 56 atomic percent; Co in the amount of 0 to 7 atomic percent; Mn in the amount of 0 to 8.5 atomic percent; Al in the amount of 0. to 3 atomic percent; Fe in the amount of 0 to 2.5 atomic percent; Mo in the amount of 0 to 6.2 atomic percent; La in the amount of 0 to 30 atomic percent; and Mm in the amount of 0 to 30 atomic percent;

where the total amount of said elements is equal to 100 atomic percent of said second material; and blending said first component and said second component together by mechanically mixing using ball milling, or impact mixing to form non-uniform heterogeneous powder particles.

18. The method of making non-uniform heterogeneous composite powder particles of claim 17, where said second component comprises an alloy of the following composition:

19. The method of making non-uniform heterogeneous composite powder particles of claim 17 where said first component comprises an alloy of the following composition:

## (Base Alloy)<sub>a</sub> M<sub>b</sub>

40

45

50

55

where,

Base Alloy is an alloy of Mg and Ni in a ratio of from about 1:2 to about 2:1;

M represents at least one modifier element chosen from the group consisting of Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li. Cd, Na, Pb, La, Ce, Pr, Nd, Mm, and Ca; b is greater than 0.5 and less than 30 atomic percent; and

a+b=100 atomic percent of said first component material..

- 20. Non-uniform heterogeneous composite powder particles of claim 1 for use as active material for a nickel metal hydride negative electrode comprising a composite material formed from single phase or multiple phase Mg base alloys blended together with at least one member selected from the group consisting of single phase TiNi alloys, single phase LaNi<sub>5</sub> alloys, multiple phase TiNi alloys, and multiple phase LaNi<sub>5</sub> alloys.
- 21. The non-uniform heterogeneous composite powder particles of claim 20, where said composite material comprises at least two separate and distinct alloy components when distinguished on the micron level.
- 22. The non-uniform heterogeneous composite powder particles of claim 20, where said composite material has a lamellar structure.

23. A metal hydride negative electrode having an active material comprising:

non-uniform heterogeneous composite powder particles comprising a composite material formed from single phase or multiple phase Mg base alloys blended together with at least one member selected from the group consisting of single phase TiNi alloys, single phase LaNi<sub>5</sub> alloys, multiple phase TiNi alloys, and multiple phase LaNi<sub>5</sub> alloys.

- 24. The metal hydride negative electrode of claim 23, where said non-uniform heterogeneous composite powder particles comprise at least two separate and distinct alloy components when distinguished on the micron level.
- 25. The metal hydride negative electrode of claim 24, where said non-uniform heterogeneous composite powder particles have a lamellar structure.
- 26. The metal hydride negative electrode of claim 23, wherein said non-uniform heterogeneous composite powder particles comprising a first alloy blended with a second alloy comprises a first alloy having the following composition:.

20 where,

5

10

15

25

30

35

40

50

M represents at least one modifier element chosen from the group consisting of Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, and Ca;

b ranges from 0 to less than 30 atomic percent; and

a+b=100 atomic percent of said first component;

 $0.25 \le x \le 0.75$ ; and

a second alloy having at least one element chosen from the group consisting of:

Ti in the amount of 0 to 60 atomic percent; Zr in the amount of 0 to 40 atomic percent; V in the amount of 0 to 60 atomic percent; Ni in the amount of 0 to 57 atomic percent; Cr in the amount of 0 to 56 atomic percent; Cu in the amount of 0 to 56 atomic percent; Co in the amount of 0 to 15 atomic percent; Mn in the amount of 0 to 20 atomic percent; Al in the amount of 0 to 20 atomic percent; Fe in the amount of 0 to 10 atomic percent; Mo in the amount of 0 to 8 atomic percent; La in the amount of 0 to 30 atomic percent; and Mm in the amount of 0 to 30 atomic percent;

where the total amount of said elements is equal to 100 atomic percent of said second component.

- 27. The metal hydride negative electrode of claim 26, where said second component encapsulates said first component.
  - 28. The metal hydride negative electrode of claim 26, where said second component is present as intimately mixed striations of said first component.
  - 29. The metal hydride negative electrode of claim 26, where said powder particles comprise blended composite powder particles of said second component and said first component.
- 30. The metal hydride negative electrode of claim 26, where said non-uniform heterogeneous composite powder particles exhibit a preferential distribution of said second component on their surface.
  - 31. The metal hydride negative electrode of claim 26, where said second component comprises a disordered multicomponent material comprising the following elements:

Ti in the amount of 0.1 to 60 atomic percent; Zr in the amount of 0.1 to 25 atomic percent; V in the amount of 0 to 60 atomic percent; Ni in the amount of 0.1 to 57 atomic percent; Cr in the amount of 0.1 to 56 atomic percent; Co in the amount of 0 to 7 atomic percent; Mn in the amount of 4.5 to 8.5 atomic percent; Al in the amount of 0. to 3 atomic percent; Fe in the amount of 0 to 2.5 atomic percent; Mo in the amount of 0 to 6.5 atomic percent; La in the amount of 0 to 30 atomic percent; and Mm in the amount of 0 to 30 atomic percent;

where the total amount of said elements is equal to 100 atomic percent of said second component.

32. The metal hydride negative electrode of claim 26, where said second component comprises an alloy of the following composition:

V<sub>18</sub>Ti<sub>15</sub>Zr<sub>18</sub>Ni<sub>29</sub>Cr<sub>5</sub>Co<sub>7</sub>Mn<sub>8</sub>.

33. An electrochemical hydrogen storage cell comprising: non-uniform heterogeneous composite powder particles for electrochemical hydrogen storage comprising:

a first component comprising materials having the following composition:

(Mg<sub>x</sub> Ni<sub>1-x</sub>)<sub>a</sub> M<sub>b</sub>

30 where,

10

15

20

25

35

40

45

50

55

M represents at least one modifier element chosen from the group consisting of Ni, Co,-Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, and Ca;

b ranges from 0 to less than 30 atomic percent; and

a+b=100 atomic percent of said first component material; 0.25 ≤ x ≤ 0.75; blended with

a second component comprising at least one element chosen from the group consisting of:

Ti in the amount of 0 to 60 atomic percent: Zr in the amount of 0 to 40 atomic percent: V in the amount of 0 to 60 atomic percent; Ni in the amount at 0 to 57 atomic percent; Cr in the amount of 0 to 5 atomic percent: Cu in the amount of 0 to 56 atomic percent; Co in the amount of 0 to 15 atomic percent; Mn in the amount of 0 to 20 atomic percent; Al in the amount of 0 to 20 atomic percent: Fe in the amount of 0 to 10 atomic percent; Mo in the amount of 0 to 8 atomic percent; La in the amount of 0 to 30 atomic percent; and Mm in the amount of 0 to 30 atomic percent;

where the total amount of said elements is equal to 100 atomic percent of said second component.

## Patentansprüche

 Uneinheitliche heterogene zusammengesetzte Pulverteilchen für elektrochemische Verwendungen, wo jedes der benannten uneinheitlichen, heterogenen zusammengesetzten Pulverteilchen zumindest zwei getrennte und unterschiedliche, zusammengemische Wasserstoffspeicherlegierungen umfasst und wo eine der benannten, zumin-

dest zwei getrennten und unterschiedlichen Wasserstoffspeicherlegierungen eine Legierung auf Mg-Basis ist.

- 2. Die uneinheitlichen heterogenen zusammengesetzten Pulverteilchen des Anspruchs 1, worin die benannten uneinheitlichen, heterogenen zusammengesetzten Pulverteilen zumindest zwei getrennte und unterschiedliche Legierungskomponenten umfassen, wenn im Mikrometermassstab gekennzeichnet.
- 3. Die uneinheitlichen heterogenen zusammengesetzten Pulverteilchen des Anspruchs 2, worin die benannten uneinheitlichen, heterogenen zusammengesetzten Pulverteilchen eine lamellenartige Struktur haben.
- 4. Die uneinheitlichen heterogenen zusammengesetzten Pulverteilchen des Anspruchs 1, wo eine erste Legierung der benannten, zumindest zwei getrennten und unterschiedlichen Wasserstoffspeicherlegierungen Materialien der folgenden Zusammensetzung umfasst:

 $(Mg_xNi_{1-x})_aM_b$ 

wo

M zumindest ein Modifikatorelement darstellt, das aus der Gruppe gewählt ist, die aus Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm und Ca besteht;

b im Bereich von 0 bis weniger als 30 Atomprozent liegt; und

a + b = 100 Atomprozent der benannten ersten Legierung;

 $0.25 \le x \le 0.75$ ; und

wo eine zweite Legierung der benannten, zumindest zwei getrennten und unterschiedlichen Wasserstoffspeicherlegierungen Komponenten umfasst, die aus einer Gruppe gewählt sind, die besteht aus:

25

30

35

45

5

15

20

Ti in einer Menge von 0 bis 60 Atomprozent;
Zr in einer Menge von 0 bis 40 Atomprozent;
V in einer Menge von 0 bis 60 Atomprozent;
Ni in einer Menge von 0 bis 57 Atomprozent;
Cr in einer Menge von 0 bis 56 Atomprozent;
Cu in einer Menge von 0 bis 56 Atomprozent;
Co in einer Menge von 0 bis 15 Atomprozent;
Mn in einer Menge von 0 bis 20 Atomprozent;
Al in einer Menge von 0 bis 20 Atomprozent;
Fe in einer Menge von 0 bis 10 Atomprozent;
Mo in einer Menge von 0 bis 8 Atomprozent;
La in einer Menge von 0 bis 30 Atomprozent; und

Mm in einer Menge von 0 bis 30 Atomprozent;

- wo die Gesamtmenge der benannten Komponenten 100 Atomprozent der benannten zweiten Legierung beträgt.
  - 5. Uneinheitliche heterogene zusammengesetzte Pulverteilchen für elektrochemische Verwendungen, wobei die benannten Pulverteilchen zumindest zwei getrennte und unterschiedliche Wasserstoffspeicherlegierungen umfassen, wo eine erste Legierung der benannten, zumindest zwei getrennten und unterschiedlichen Wasserstoffspeicherlegierungen Materialien umfasst, die die folgende Zusammensetzung haben:

 $(Mg_xNi_{1-x})_aM_b$ 

50 wo

M zumindest ein Modifikatorelement darstellt, das aus der Gruppe gewählt ist, die aus Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm und Ca besteht;

b im Bereich von 0 bis weniger als 30 Atomprozent liegt; und

a + b = 100 Atomprozent der benannten ersten Legierung;

 $0,25 \le x \le 0,75$ ; und

wo eine zweite Legierung der benannten, zumindest zwei getrennten und unterschiedlichen Wasserstoffspeicherlegierungen Komponenten umfasst, die aus einer Gruppe gewählt sind, die besteht aus:

Ti in einer Menge von 0 bis 60 Atomprozent; V in einer Menge von 0 bis 60 Atomprozent; Zr in einer Menge von 0 bis 40 Atomprozent; Ni in einer Menge von 0 bis 57 Atomprozent; Cr in einer Menge von 0 bis 56 Atomprozent; Cu in einer Menge von 0 bis 56 Atomprozent; Co in einer Menge von 0 bis 56 Atomprozent; Mn in einer Menge von 0 bis 20 Atomprozent; Al in einer Menge von 0 bis 20 Atomprozent; Fe in einer Menge von 0 bis 10 Atomprozent; Mo in einer Menge von 0 bis 8 Atomprozent; La in einer Menge von 0 bis 30 Atomprozent; und Mm in einer Menge von 0 bis 30 Atomprozent;

10

20

30

35

40

45

50

55

- wo die Gesamtmenge der benannten Komponenten 100 Atomprozent der benannten zweiten Legierung beträgt; und die benannte zweite Legierung die benannte erste Legierung verkapselt.
  - Die uneinheitlichen heterogenen zusammengesetzten Pulverteilchen des Anspruchs 5, wo die benannte zweite Legierung als innig vermischte Schichtungen mit der benannten ersten Legierung vorliegt.
  - Das uneinheitliche heterogene zusammengesetzte Pulver des Anspruchs 5, wo die benannten Pulverteilchen vermische zusammengesetzte Pulverteilchen der benannten zweiten Legierung und der benannten ersten Legierung umfassen.
- 8. Die uneinheitlichen heterogenen zusammengesetzten Pulverteilchen des Anspruchs 5, wo die benannten Pulverteilchen eine bevorzugte Verteilung der benannten zweiten Legierung auf ihrer Oberfläche aufweisen.
  - Die uneinheitlichen heterogenen zusammengesetzten Pulverteilchen des Anspruchs 5, wo das benannte zweite Legierungsmaterial ein ungeordnetes Vielkomponentenmaterial umfasst, das die folgenden Komponenten umfasst:

Ti in einer Menge von 0,1 bis 60 Atomprozent; Zr in einer Menge von 0,1 bis 25 Atomprozent; V in einer Menge von 0 bis 60 Atomprozent; Ni in einer Menge von 0,1 bis 57 Atomprozent; Cr in einer Menge von 0,1 bis 56 Atomprozent; Co in einer Menge von 0 bis 7 Atomprozent; Mn in einer Menge von 4,5 bis 8,5 Atomprozent; Al in einer Menge von 0, bis 3 Atomprozent; Fe in einer Menge von 0 bis 2,5 Atomprozent; Mo in einer Menge von 0 bis 5,5 Atomprozent; La in einer Menge von 0 bis 30 Atomprozent; und Mm in einer Menge von 0 bis 30 Atomprozent;

- wo die Gesamtmenge der benannten Komponenten 100 Atomprozent des benannten zweiten Komponentenmaterials beträgt.
- 10. Die uneinheitlichen heterogenen zusammengesetzten Pulverteilchen des Anspruchs 5, wo die benannte zweite Legierung die folgende Zusammensetzung hat:

V<sub>18</sub>Ti<sub>15</sub>Zr<sub>18</sub>Ni<sub>29</sub>Cr<sub>5</sub>Co<sub>7</sub>Mn<sub>8</sub>.

11. Die uneinheitlichen heterogenen zusammengesetzten Pulverteilchen des Anspruchs 5, wo die benannte erste Legierung die folgende Zusammensetzung hat:

(Basislegierung)<sub>a</sub>M<sub>b</sub>,

wo

Basislegierung eine Legierung von Mg und Ni in einem Verhältnis ist, das von etwa 1:2 bis etwa 2:1 reicht; M zumindest ein Modifikatorelement darstellt, das aus der Gruppe gewählt ist, die aus Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm und Ca besteht; b grösser als 0,5 Atomprozent und kleiner als 30 Atomprozent ist; und

a + b = 100 Atomprozent des benannten ersten Komponentenmaterials.

12. Verfahren zur Herstellung uneinheitlicher heterogener zusammengesetzter Pulverteilchen für elektrochemische Wasserstoffspeicherung, umfassend:

10

15

20

5

eine erste Komponente durch Mischen und Schmelzen zu bilden, wo die benannte Legierung die folgende Zusammensetzung hat:

 $(Mg_xNi_{1-x})_aM_b$ 

wo

M zumindest ein Modifikatorelement darstellt, das aus der Gruppe gewählt ist, die aus Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm und Ca besteht;

b im Bereich von 0 bis weniger als 30 Atomprozent liegt; und

a + b = 100 Atomprozent des benannten ersten Komponentenmaterials;

 $0.25 \le x \le 0.75$ ; und

eine zweite Komponente zu bilden, die zumindest ein Element umfasst, das aus der Gruppe gewählt ist, die besteht aus:

25

30

Ti in einer Menge von 0 bis 60 Atomprozent; Zr in einer Menge von 0 bis 40 Atomprozent; V in einer Menge von 0 bis 60 Atomprozent; Ni in einer Menge von 0 bis 57 Atomprozent; Cr in einer Menge von 0 bis 56 Atomprozent; Cu in einer Menge von 0 bis 56 Atomprozent; Co in einer Menge von 0 bis 15 Atomprozent; Mn in einer Menge von 0 bis 20 Atomprozent; Al in einer Menge von 0 bis 20 Atomprozent; Fe in einer Menge von 0 bis 10 Atomprozent; Mo in einer Menge von 0 bis 8 Atomprozent;

35

La in einer Menge von 0 bis 30 Atomprozent; und Mm in einer Menge von 0 bis 30 Atomprozent;

40

45

55

wo die Gesamtmenge der benannten Komponenten 100 Atomprozent des benannten zweiten Komponentenmaterials beträgt;

die benannte erste Komponente mit der benannten zweiten Komponente zu verkapseln.

- 13. Verfahren, uneinheitliche heterogene zusammengesetzte Pulverteilchen für elektrochemische Wasserstoffspeicherung des Anspruchs 12 herzustellen, wo der benannte Verkapselungsschritt unter Verwendung eines Verfahrens ausgeführt wird, das aus der Gruppe ausgewählt ist, die aus Schmelzspinnen, Gasatomisierung, Ultraschallatomisierung, Zentrifugalatomisierung, Planar Flow Casting, Plasmasprühen, mechanisches Legieren und Abscheidung aus der Dampfphase besteht.
- 14. Verfahren, uneinheitliche heterogene zusammengesetzte Pulverteilchen für elektrochemische Wasserstoffspei-50 cherung des Anspruchs 12 herzustellen, wo die benannte zweite Komponente ein ungeordnetes Vielkomponentenmaterial umfasst, das die folgenden Elemente umfasst:

Ti in einer Menge von 0,1 bis 60 Atomprozent; Zr in einer Menge von 0,1 bis 25 Atomprozent; V in einer Menge von 0 bis 60 Atomprozent; Ni in einer Menge von 0,1 bis 57 Atomprozent; Cr in einer Menge von 0,1 bis 56 Atomprozent;

Co in einer Menge von 0 bis 7 Atomprozent; Mn in einer Menge von 4,5 bis 8,5 Atomprozent; Al in einer Menge von 0, bis 3 Atomprozent; Fe in einer Menge von 0 bis 2,5 Atomprozent; Mo in einer Menge von 0 bis 6,5 Atomprozent; La in einer Menge von 0 bis 30 Atomprozent; und Mm in einer Menge von 0 bis 30 Atomprozent;

wo die Gesamtmenge der benannten Elemente 100 Atomprozent der benannten zweiten Komponente beträgt.

15. Verfahren, uneinheitliche heterogene zusammengesetzte Pulverteilchen für elektrochemische Wasserstoffspeicherung des Anspruchs 12 herzustellen, wo die benannte zweite Komponente eine Legierung der folgenden Zusammensetzung umfasst:

V<sub>18</sub>Ti<sub>15</sub>Zr<sub>18</sub>Ni<sub>29</sub>Cr<sub>5</sub>Co<sub>7</sub>Mn<sub>8</sub>.

16. Verfahren, uneinheitliche heterogene zusammengesetzte Pulverteilchen für elektrochemische Wasserstoffspeicherung des Anspruchs 12 herzustellen, wo die benannte erste Komponente eine Legierung der folgenden Zusammensetzung umfasst:

(Basislegierung)<sub>a</sub>M<sub>b</sub>,

wo
 Basislegierung eine Legierung von Mg und Ni in einem Verhältnis ist, das von etwa 1:2 bis etwa 2:1 reicht;
 M zumindest ein Modifikatorelement darstellt, das aus der Gruppe gewählt ist, die aus Co, Mn, Al, Fe, Cu, Mo, W,
 Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm und Ca besteht;
 b grösser als 0,5 Atomprozent und kleiner als 30 Atomprozent ist; und
 a + b = 100 Atomprozent der benannten ersten Komponente.

- 17. Verfahren, uneinheitliche heterogene zusammengesetzte Pulverteilchen für elektrochemische Wasserstoffspeicherung herzustellen, die Schritte umfassend:
- 35 eine erste Komponente zu bilden, die die folgende Zusammensetzung hat:

 $(Mg_xNi_{1-x})_aM_b$ 

40 WO

50

55

10

15

20

M zumindest ein Modifikatorelement darstellt, das aus der Gruppe gewählt ist, die aus Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm und Ca besteht;

b im Bereich von 0 bis weniger als 30 Atomprozent liegt; und

a + b = 100 Atomprozent des benannten ersten Komponentenmaterials;

45  $0,25 \le x \le 0,75$ ; und

eine zweite Komponente zu bilden, die ein ungeordnetes Vielkomponentenmaterial ist, das die folgenden Elemente umfasst:

Ti in einer Menge von 0,1 bis 60 Atomprozent;
Zr in einer Menge von 0,1 bis 25 Atomprozent;
V in einer Menge von 0 bis 60 Atomprozent;
Ni in einer Menge von 0,1 bis 57 Atomprozent;
Cr in einer Menge von 0,1 bis 56 Atomprozent;
Co in einer Menge von 0 bis 7 Atomprozent;
Mn in einer Menge von 4,5 bis 8,5 Atomprozent;
Al in einer Menge von 0, bis 3 Atomprozent;
Fe in einer Menge von 0 bis 2,5 Atomprozent;
Mo in einer Menge von 0 bis 6,2 Atomprozent;

La in einer Menge von 0 bis 30 Atomprozent; und Mm in einer Menge von 0 bis 30 Atomprozent;

wo die Gesamtmenge der benannten Elemente 100 Atomprozent des benannten zweiten Materials beträgt; und die benannte erste Komponente und die benannte zweite Komponente zusammengemischt werden durch mechanisches Mischen unter Einsatz des Kugelmahlens oder Hammermühlmischens, um uneinheitliche heterogene Pulverteilchen zu bilden.

18. Verfahren zur Herstellung uneinheitlicher heterogener zusammengesetzter Pulverteilchen des Anspruchs 17, wo die benannte zweite Komponente eine Legierung der folgenden Zusammensetzung umfasst:

$$V_{18}Ti_{15}Zr_{18}Ni_{29}Cr_5Co_7Mn_8$$
.

19. Verfahren zur Herstellung uneinheitlicher heterogener zusammengesetzter Pulverteilchen des Anspruchs 17, worin die benannte erste Komponente eine Legierung der folgenden Zusammensetzung umfasst:

(Basislegierung)<sub>a</sub>M<sub>b</sub>,

wo

5

10

15

20

25

30

40

45

50

55

Basislegierung eine Legierung von Mg und Ni in einem Verhältnis ist, das von etwa 1:2 bis etwa 2:1 reicht; M zumindest ein Modifikatorelement darstellt, das aus der Gruppe gewählt ist, die aus Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm und Ca besteht; b grösser als 0,5 Atomprozent und kleiner als 30 Atomprozent ist; und

- a + b = 100 Atomprozent des benannten ersten Komponentenmaterials.
- 20. Uneinheitliche heterogene zusammengesetzte Pulverteilchen des Anspruchs 1 zur Verwendung als aktives Material für eine negative Nickel-Metallhydridelektrode, ein zusammengesetztes Material umfassend, das gebildet ist aus einphasigen oder mehrphasigen Legierungen auf Mg-Basis, zusammengemischt mit zumindest einem Glied, das aus der Gruppe ausgewählt ist, die aus einphasigen TiNi-Legierungen, einphasigen LaNi<sub>5</sub>-Legierungen, mehrphasigen TiNi-Legierungen und mehrphasigen LaNi<sub>5</sub>-Legierungen besteht.
- 21. Die uneinheitlichen heterogenen zusammengesetzten Pulverteilchen des Anspruchs 20, wo das benannte zusammengesetzte Material zumindest zwei getrennte und unterschiedliche Legierungskomponenten umfasst, wenn im Mikrometermassstab gekennzeichnet.
  - 22. Die uneinheitlichen heterogenen zusammengesetzten Pulverteilchen des Anspruchs 20, wo das benannte zusammengesetzte Material eine lamellenartige Struktur hat.
  - 23. Negative Metallhydridelektrode mit einem aktiven Material, umfassend:

uneinheitliche heterogene zusammengesetzte Pulverteilchen, ein zusammengesetztes Material umfassend, das aus einphasigen oder mehrphasigen Legierungen auf Mg-Basis gebildet ist, die mit zumindest einem Glied zuammengemischt sind, das aus der Gruppe ausgewählt ist, die aus einphasigen TiNi-Legierungen, einphasigen LaNi<sub>5</sub>-Legierungen, mehrphasigen TiNi-Legierungen und mehrphasigen LaNi<sub>5</sub>-Legierungen besteht.

- 24. Die negative Metallhydridelektrode des Anspruchs 23, wo die benannten uneinheitlichen heterogenen zusammengesetzten Pulverteilchen zumindest zwei getrennte und unterschiedliche Legierungskomponenten umfassen, wenn im Mikrometermassstab gekennzeichnet.
  - 25. Die negative Metallhydridelektrode des Anspruchs 24, wo die benannten uneinheitlichen heterogenen zusammengesetzten Pulverteilchen eine lamellenartige Struktur haben.
  - 26. Die negative Metallhdridelektrode des Anspruchs 23, wo die benannten uneinheitlichen heterogenen zusammengesetzten Pulverteilchen, die eine mit einer zweiten Legierung vermischte erste Legierung umfassen, eine erste Legierung umfassen, die die folgende Zusammensetzung hat:

 $(Mg_xNi_{1-x})_aM_b$ 

wo

5

10

15

20

25

35

45

50

55

M zumindest ein Modifikatorelement darstellt, das aus der Gruppe gewählt ist, die aus Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm und Ca besteht; b im Bereich von 0 bis weniger als 30 Atomprozent liegt; und

a + b = 100 Atomprozent der benannten ersten Komponente;

 $0.25 \le x \le 0.75$ ; und

eine zweite Legierung, die zumindest ein Element hat, das aus der Gruppe gewählt ist, die besteht aus:

Ti in einer Menge von 0 bis 60 Atomprozent;
Zr in einer Menge von 0 bis 40 Atomprozent;
V in einer Menge von 0 bis 60 Atomprozent;
Ni in einer Menge von 0 bis 57 Atomprozent;
Cr in einer Menge von 0 bis 56 Atomprozent;
Cu in einer Menge von 0 bis 56 Atomprozent;
Co in einer Menge von 0 bis 15 Atomprozent;
Mn in einer Menge von 0 bis 20 Atomprozent;
Al in einer Menge von 0 bis 20 Atomprozent;
Fe in einer Menge von 0 bis 30 Atomprozent;
La in einer Menge von 0 bis 30 Atomprozent; und
Mm in einer Menge von 0 bis 30 Atomprozent;

wo die Gesamtmenge der benannten Elemente 100 Atomprozent der benannten zweiten Komponente beträgt.

- 27. Die negative Metallhydridelektrode des Anspruchs 26, wo die benannte zweite Komponente die benannte erste Komponente verkapselt.
- 28. Die negative Metallhydridelektrode des Anspruchs 26, wo die benannte zweite Komponente als innig vermischte Schichtungen der benannten ersten Komponente vorliegt.
  - 29. Die negative Metallhydridelektrode des Anspruchs 26, wo die benannten Pulverteilchen vermischte zusammengesetzte Pulverteilchen der benannten zweiten Komponente und der benannten ersten Komponente umfassen.
  - 30. Die negative Metallhydridelektrode des Anspruchs 26, wo die benannten uneinheitlichen heterogenen zusammengesetzten Pulverteilchen eine bevorzugte Verteilung der benannten zweiten Komponente auf ihrer Oberfläche aufweisen.
- 31. Die negative Metallhydridelektrode des Anspruchs 26, wo die benannte zweite Komponente ein ungeordnetes Vielkomponentenmaterial umfasst, das die folgenden Elemente umfasst:

Ti in einer Menge von 0,1 bis 60 Atomprozent;

Zr in einer Menge von 0,1 bis 25 Atomprozent;

V in einer Menge von 0 bis 60 Atomprozent;

Ni in einer Menge von 0,1 bis 57 Atomprozent;

Cr in einer Menge von 0,1 bis 56 Atomprozent;

Co in einer Menge von 0 bis 7 Atomprozent; Mn in einer Menge von 4,5 bis 8,5 Atomprozent;

Al in einer Menge von 0, bis 3 Atomprozent;

Fe in einer Menge von 0 bis 2,5 Atomprozent;

Mo in einer Menge von 0 bis 6,5 Atomprozent;

La in einer Menge von 0 bis 30 Atomprozent; und

Mm in einer Menge von 0 bis 30 Atomprozent; wo die Gesamtmenge der benannten Elemente 100 Atomprozent der benannten zweiten Komponente beträgt.

32. Die negative Metallhydridelektrode des Anspruchs 26, wo die benannte zweite Komponente eine Legierung der folgenden Zusammensetzung umfasst:

V<sub>18</sub>Ti<sub>15</sub>Zr<sub>18</sub>Ni<sub>29</sub>Cr<sub>5</sub>Co<sub>7</sub>Mn<sub>8</sub>.

**33.** Elektrochemische Wasserstoffspeicherzelle, umfassend: uneinheitliche heterogene zusammengesetzte Pulverteilchen für elektrochemische Wasserstoffspeicherung, umfassend:

eine erste Komponente, Materialien der folgenden Zusammensetzung umfassend:

(Mg<sub>x</sub>Ni<sub>1-x</sub>)<sub>a</sub>M<sub>b</sub>,

10

15

20

25

30

35

40

45

55

M zumindest ein Modifikatorelement darstellt, das aus der Gruppe gewählt ist, die aus Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm und Ca besteht;

b im Bereich von 0 bis weniger als 30 Atomprozent liegt; und

a + b = 100 Atomprozent des benannten ersten Komponentenmaterials; 0,25  $\le$  x  $\le$  0,75; vermischt mit einer zweiten Komponente, die zumindest ein Element umfasst, das aus der Gruppe gewählt ist, die besteht aus:

Ti in einer Menge von 0 bis 60 Atomprozent; Zr in einer Menge von 0 bis 40 Atomprozent; V in einer Menge von 0 bis 60 Atomprozent; Ni in einer Menge von 0 bis 57 Atomprozent; Cr in einer Menge von 0 bis 5 Atomprozent; Cu in einer Menge von 0 bis 56 Atomprozent; Co in einer Menge von 0 bis 56 Atomprozent; Co in einer Menge von 0 bis 20 Atomprozent; Mn in einer Menge von 0 bis 20 Atomprozent; Al in einer Menge von 0 bis 20 Atomprozent; Fe in einer Menge von 0 bis 30 Atomprozent; La in einer Menge von 0 bis 30 Atomprozent; und Mm in einer Menge von 0 bis 30 Atomprozent;

wo die Gesamtmenge der benannten Elemente 100 Atomprozent der benannten zweiten Komponente beträgt.

#### Revendications

- 1. Particules de poudre composite hétérogène non uniforme destinées à des utilisations électrochimiques, où chacune desdites particules de poudre composite hétérogène non uniforme comprend au moins deux alliages de stockage d'hydrogène séparés et distincts mélangés ensemble et où l'un desdits au moins deux alliages de stockage d'hydrogène séparés et distincts est un alliage à base de Mg.
- 2. Particules de poudre composite hétérogène non uniforme selon la revendication 1, dans lesquelles lesdites particules de poudre composite hétérogène non uniforme comprennent deux composants d'alliages séparés et distincts lorsque l'on fait la distinction au niveau micrométrique.
- 3. Particules de poudre composite hétérogène non uniforme selon la revendication 2, dans lesquelles lesdites particules de poudre composite hétérogène non uniforme présentent une structure lamellaire.
- 4. Particules de poudre composite hétérogène non uniforme selon la revendication 1, où un premier alliage desdits au moins deux alliages de stockage d'hydrogène séparés et distincts comprend des matériaux présentant la composition suivante :

 $(Mg_vNi_{1-v})_aM_b$ 

où,

M représente au moins un élément modificateur choisi parmi le groupe constitué de Ni, Co, Mn, Al, Fe, Cu,

Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, et Ca,

b va de 0 à moins de 30 pour cent atomique, et

a + b = 100 pour cent atomique dudit premier alliage,

 $0.25 \le x \le 0.75$ , et

où un second alliage desdits au moins deux alliages de stockage d'hydrogène séparés et distincts comprend des composants choisis parmi un groupe constitué de :

Ti dans la proportion de 0 à 60 pour cent atomique, Zr dans la proportion de 0 à 40 pour cent atomique, V dans la proportion de 0 à 60 pour cent atomique, Ni dans la proportion de 0 à 57 pour cent atomique, Cr dans la proportion de 0 à 56 pour cent atomique, Cu dans la proportion de 0 à 56 pour cent atomique, Co dans la proportion de 0 à 15 pour cent atomique, Mn dans la proportion de 0 à 20 pour cent atomique, Al dans la proportion de 0 à 20 pour cent atomique, Fe dans la proportion de 0 à 10 pour cent atomique, Mo dans la proportion de 0 à 8 pour cent atomique, La dans la proportion de 0 à 30 pour cent atomique, et Mm dans la proportion de 0 à 30 pour cent atomique, et Mm dans la proportion de 0 à 30 pour cent atomique,

où la proportion totale desdits composants est égale à 100 pour cent atomique dudit second alliage.

5. Particules de poudre composite hétérogène non uniforme destinées à des utilisations électrochimiques, lesdites particules de poudre comprenant au moins deux alliages de stockage d'hydrogène séparés et distincts où un premier alliage desdits au moins deux alliages de stockage d'hydrogène séparés et distincts comprend des matériaux présentant la composition suivante :

 $(Mg_xNi_{1-x})_aM_b$ 

оù,

M représente au moins un élément modificateur choisi parmi le groupe constitué de Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, et Ca,

B va de 0 à moins de 30 pour cent atomique, et

a + b = 100 pour cent atomique dudit premier alliage,

 $0,25 \le x \le 0,75$ , et

où un second alliage desdits au moins deux alliages de stockage d'hydrogène séparés et distincts comprend des composants choisis parmi un groupe constitué de :

40

45

5

10

15

20

25

30

35

Ti dans la proportion de 0 à 60 pour cent atomique, V dans la proportion de 0 à 60 pour cent atomique, Zr dans la proportion de 0 à 40 pour cent atomique, Ni dans la proportion de 0 à 57 pour cent atomique, Cr dans la proportion de 0 à 56 pour cent atomique, Cu dans la proportion de 0 à 56 pour cent atomique, Co dans la proportion de 0 à 15 pour cent atomique, Mn dans la proportion de 0 à 20 pour cent atomique, Al dans la proportion de 0 à 20 pour cent atomique, Fe dans la proportion de 0 à 10 pour cent atomique, Mo dans la proportion de 0 à 8 pour cent atomique, La dans la proportion de 0 à 30 pour cent atomique, et

Mm dans la proportion de 0 à 30 pour cent atomique,

50

55

où la proportion totale desdits composants est égale à 100 pour cent atomique dudit second alliage, et ledit second alliage encapsule ledit premier alliage.

6. Particules de poudre composite hétérogène non uniforme selon la revendication 5, où ledit second alliage est

présent sous forme de stries intimement mélangées audit premier alliage.

- 7. Particules de poudre composite hétérogène non uniforme selon la revendication 5, où lesdites particules de poudre comprennent des particules de poudre composite mélangées dudit second alliage et dudit premier alliage.
- 8. Particules de poudre composite hétérogène non uniforme selon la revendication 5, où les dites particules de poudre présentent une distribution préférentielle dudit second alliage sur leurs surfaces.
- 9. Particules de poudre composite hétérogène non uniforme selon la revendication 5, où ledit second matériau d'al 10 liage comprend un matériau à composants multiples désordonné comprenant les composants suivants :

Ti dans la proportion de 0,1 à 60 pour cent atomique, Zr dans la proportion de 0,1 à 25 pour cent atomique, V dans la proportion de 0 à 60 pour cent atomique, Ni dans la proportion de 0,1 à 57 pour cent atomique, Cr dans la proportion de 0,1 à 56 pour cent atomique, Co dans la proportion de 0 à 7 pour cent atomique, Mn dans la proportion de 4,5 à 8,5 pour cent atomique, Al dans la proportion de 0 à 3 pour cent atomique, Fe dans la proportion de 0 à 2,5 pour cent atomique, Mo dans la proportion de 0 à 5,5 pour cent atomique, La dans la proportion de 0 à 30 pour cent atomique, et Mm dans la proportion de 0 à 30 pour cent atomique, et

- 25 où la proportion totale désdits composants est égale à 100 pour cent atomique dudit second matériau de composant.
  - **10.** Particules de poudre composite hétérogène non uniforme selon la revendication 5, où ledit second alliage présente la composition suivante :

V<sub>18</sub>Ti<sub>15</sub>Zr<sub>18</sub>Ni<sub>29</sub>Cr<sub>5</sub>Co<sub>7</sub>Mn<sub>8</sub>.

11. Particules de poudre composite hétérogène non uniforme selon la revendication 5, où ledit premier alliage présente la composition suivante :

(alliage de base)<sub>a</sub>M<sub>b</sub>

40 où

5

15

20

30

35

45

50

l'alliage de base est un alliage de Mg et de Ni dans un rapport d'environ 1:2 à environ 2:1, M représente au moins un élément modificateur choisi parmi le groupe constitué de Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, et Ca,

b est supérieur à 0,5 pour cent atomique et inférieur à 30 pour cent atomique, et a + b = 100 pour cent atomique dudit premier matériau de composant.

- 12. Procédé de fabrication de particules de poudre composite hétérogène non uniforme destinées à un stockage électrochimique d'hydrogène comprenant :
  - la formation d'un premier composant par mélange et fusion où ledit alliage présente la composition suivante :

 $(Mg_xNi_{1-x})_aM_b$ 

55 où,

M représente au moins un élément modificateur choisi parmi le groupe constitué de Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, et Ca, b va de 0 à moins de 30 pour cent atomique,

a + b = 100 pour cent atomique dudit premier matériau de composant,  $0.25 \le x \le 0.75$ , et

la formation d'un second composant comprenant au moins un élément choisi parmi le groupe constitué de :

Ti dans la proportion de 0 à 60 pour cent atomique, Zr dans la proportion de 0 à 40 pour cent atomique, V dans la proportion de 0 à 60 pour cent atomique, Ni dans la proportion de 0 à 57 pour cent atomique, Cr dans la proportion de 0 à 56 pour cent atomique, Cu dans la proportion de 0 à 56 pour cent atomique, Co dans la proportion de 0 à 15 pour cent atomique, Mn dans la proportion de 0 à 20 pour cent atomique, Al dans la proportion de 0 à 20 pour cent atomique, Fe dans la proportion de 0 à 10 pour cent atomique, Mo dans la proportion de 0 à 8 pour cent atomique, La dans la proportion de 0 à 30 pour cent atomique, et Mm dans la proportion de 0 à 30 pour cent atomique, et Mm dans la proportion de 0 à 30 pour cent atomique,

5

10

15

20

25

30

35

40

45

50

55

où la proportion totale desdits composants est égale à 100 pour cent atomique dudit second matériau de composant,

l'encapsulation dudit premier composant par ledit second composant.

- 13. Procédé de fabrication de particules de poudre composite hétérogène non uniforme destinées à un stockage électrochimique d'hydrogène selon la revendication 12, où ladite étape d'encapsulation est réalisée en utilisant un procédé choisi parmi un groupe constitué d'une filature en fusion, d'une atomisation de gaz, d'une atomisation par ultrasons, d'une atomisation centrifuge, d'un moulage plan par absorption, d'une pulvérisation de plasma, d'un alliage mécanique et d'un dépôt en phase vapeur.
- 14. Procédé de fabrication de particules de poudre composite hétérogène non uniforme destinées à un stockage électrochimique d'hydrogène selon la revendication 12, où ledit second composant comprend un matériau à composants multiples désordonné comprenant les éléments suivants :

Ti dans la proportion de 0,1 à 60 pour cent atomique, Zr dans la proportion de 0,1 à 25 pour cent atomique, V dans la proportion de 0 à 60 pour cent atomique, Ni dans la proportion de 0,1 à 57 pour cent atomique, Cr dans la proportion de 0,1 à 56 pour cent atomique, Co dans la proportion de 0 à 7 pour cent atomique, Mn dans la proportion de 4,5 à 8,5 pour cent atomique, Al dans la proportion de 0 à 3 pour cent atomique, Fe dans la proportion de 0 à 2,5 pour cent atomique, Mo dans la proportion de 0 à 6,5 pour cent atomique, La dans la proportion de 0 à 30 pour cent atomique, et Mm dans la proportion de 0 à 30 pour cent atomique,

où la proportion totale desdits éléments est égale à 100 pour cent atomique dudit second composant.

15. Procédé de fabrication de particules de poudre composite hétérogène non uniforme destinées à un stockage électrochimique d'hydrogène selon la revendication 12, où ledit second composant comprend un alliage de la composition suivante :

## V<sub>18</sub>Ti<sub>15</sub>Zr<sub>18</sub>Ni<sub>29</sub>Cr<sub>5</sub>Co<sub>7</sub>Mn<sub>8</sub>.

16. Procédé de fabrication de particules de poudre composite hétérogène non uniforme destinées à un stockage électrochimique d'hydrogène selon la revendication 12, où ledit premier composant comprend un alliage de la composition suivante :

# (alliage de base)<sub>a</sub>M<sub>b</sub>

οù.

où, l'alliage de base est un alliage de Mg et de Ni dans un rapport d'environ 1:2 à environ 2:1, M représente au moins un élément modificateur choisi parmi le groupe constitué de Co, Mn, Al, Fe, Cu, Mo,

W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, et Ca,

b est supérieur à 0,5 pour cent atomique et inférieur à 30 pour cent atomique, et

a + b = 100 pour cent atomique dudit premier composant.

10

5

17. Procédé de fabrication de particules de poudre composite hétérogène non uniforme destinées à un stockage électrochimique d'hydrogène comprenant les étapes consistant à :

former un premier composant présentant la composition suivante :

15

$$(Mg_xNi_{1-x})_aM_b$$

20

M représente au moins un élément modificateur choisi parmi le groupe constitué de Ni, Co, Mn, Al, Fe, Cu, оù, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, et Ca,

b va de 0 à moins de 30 pour cent atomique,

a + b = 100 pour cent atomique dudit premier matériau de composant,

 $0,25 \le x \le 0,75$ , et

25

former un second composant qui est un matériau à composants multiples désordonné comprenant les éléments suivants:

30

35

Ti dans la proportion de 0,1 à 60 pour cent atomique, Zr dans la proportion de 0,1 à 25 pour cent atomique, V dans la proportion de 0 à 60 pour cent atomique, Ni dans la proportion de 0,1 à 57 pour cent atomique, Cr dans la proportion de 0,1 à 56 pour cent atomique, Co dans la proportion de 0 à 7 pour cent atornique, Mn dans la proportion de 4,5 à 8,5 pour cent atomique, Al dans la proportion de 0 à 3 pour cent atomique, Fe dans la proportion de 0 à 2,5 pour cent atomique, Mo dans la proportion de 0 à 6,2 pour cent atomique, La dans la proportion de 0 à 30 pour cent atomique, et Mm dans la proportion de 0 à 30 pour cent atomique,

40

où la proportion totale desdits éléments est égale à 100 pour cent atomique dudit second matériau, et mélanger ledit premier composant et ledit second composant ensemble par un mélange mécanique en utilisant un broyeur à billes, ou par un mélange par chocs afin de former des particules de poudre hétérogène non uniforme.

45

18. Procédé de fabrication de particules de poudre composite hétérogène non uniforme selon la revendication 17, où ledit second composant comprend un alliage de la composition suivante :

 $\mathsf{V_{18}Ti_{15}Zr_{18}Ni_{29}Cr_{5}Co_{7}Mn_{8}}$ 

50

55

19. Procédé de fabrication de particules de poudre composite hétérogène non uniforme selon la revendication 17, où ledit premier composant comprend un alliage de la composition suivante :

(alliage de base)<sub>a</sub>M<sub>b</sub>

οù,

l'alliage de base est un alliage de Mg et de Ni dans un rapport d'environ 1:2 à environ 2:1, M représente au moins un élément modificateur choisi parmi le groupe constitué de Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, et Ca, b est supérieur à 0,5 et inférieur à 30 pour cent atomique, et

- a + b = 100 pour cent atomique dudit premier matériau de composant.
- 20. Particules de poudre composite hétérogène non uniforme selon la revendication 1, destinées à une utilisation en tant que matériau actif pour une électrode négative de nickel-hydrure de métal comprenant un matériau composite formé à partir d'alliages à base de Mg à une seule phase ou à phases multiples mélangés ensemble avec au moins un élément choisi parmi le groupe constitué d'alliages de TiNi à une seule phase, d'alliages de LaNi<sub>5</sub> à une seule phase, d'alliages de TiNi à phases multiples et d'alliages de LaNi<sub>5</sub> à phases multiples.
  - 21. Particules de poudre composite hétérogène non uniforme selon la revendication 1, où ledit matériau composite comprend au moins deux composants d'alliages séparés et distincts lorsque l'on fait la distinction au niveau micrométrique.
  - 22. Particules de poudre composite hétérogène non uniforme selon la revendication 20, où ledit matériau composite présente une structure lamellaire.
- 20 23. Electrode négative d'hydrure de métal comportant un matériau actif comprenant :

des particules de poudre composite hétérogène non uniforme comprenant un matériau composite formé à partir d'alliages à base de Mg à une seule phase ou à phases multiples mélangés ensemble avec au moins un élément choisi parmi le groupe constitué d'alliages de TiNi à une seule phase, d'alliages de LaNi<sub>5</sub> à une seule phase, d'alliages de TiNi à phases multiples, et d'alliages de LaNi<sub>5</sub> à phases multiples.

- 24. Electrode négative d'hydrure de métal selon la revendication 23, où lesdites particules de poudre composite hétérogène non uniforme comprennent au moins deux composants d'alliages séparés et distincts lorsque l'on fait la distinction au niveau micrométrique.
- 25. Electrode négative d'hydrure de métal selon la revendication 24, où lesdites particules de poudre composite hétérogène non uniforme présentent une structure lamellaire.
- 26. Electrode négative d'hydrure de métal selon la revendication 23, dans laquelle lesdites particules de poudre composite hétérogène non uniforme comprenant un premier alliage mélangé à un second alliage comprennent un premier alliage présentant la composition suivante :

 $(Mg_xNi_{1-x})_aM_b$ 

оù,

5

10

15

25

30

40

45

50

55

M représente au moins un élément modificateur choisi parmi le groupe constitué de Ni, Co, Mn, Al, Fe, Cu, Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, et Ca,

b va de 0 à moins de 30 pour cent atomique, et

a + b = 100 pour cent atomique dudit premier composant,

 $0.25 \le x \le 0.75$ , et

un second alliage comportant au moins un élément choisi parmi le groupe constitué de :

Ti dans la proportion de 0 à 60 pour cent atomique, Zr dans la proportion de 0 à 40 pour cent atomique, V dans la proportion de 0 à 60 pour cent atomique, Ni dans la proportion de 0 à 57 pour cent atomique, Cr dans la proportion de 0 à 56 pour cent atomique, Cu dans la proportion de 0 à 56 pour cent atomique, Co dans la proportion de 0 à 15 pour cent atomique, Mn dans la proportion de 0 à 20 pour cent atomique, Al dans la proportion de 0 à 20 pour cent atomique, Fe dans la proportion de 0 à 10 pour cent atomique,

Mo dans la proportion de 0 à 8 pour cent atomique, La dans la proportion de 0 à 30 pour cent atomique, et Mm dans la proportion de 0 à 30 pour cent atomique,

où la proportion totale desdits éléments est égale à 100 pour cent atomique dudit second composant.

- 27. Electrode négative d'hydrure de métal selon la revendication 26, où ledit second composant encapsule ledit premier composant.
- 28. Electrode négative d'hydrure de métal selon la revendication 26, où ledit second composant est présent sous forme de stries intimement mélangées audit premier composant. 10
  - 29. Electrode négative d'hydrure de métal selon la revendication 26, où lesdites particules de poudre comprennent des particules de poudre composite mélangées dudit second composant et dudit premier composant.
  - 30. Electrode négative d'hydrure de métal selon la revendication 26, où lesdites particules de poudre composite hétérogène non uniforme présentent une distribution préférentielle dudit second composant sur leurs surfaces.
- 31. Electrode négative d'hydrure de métal selon la revendication 26, où ledit second composant comprend un matériau à composants multiples désordonné comprenant les éléments suivants : 20

Ti dans la proportion de 0,1 à 60 pour cent atomique, Zr dans la proportion de 0,1 à 25 pour cent atomique, V dans la proportion de 0 à 60 pour cent atomique, Ni dans la proportion de 0,1 à 57 pour cent atomique, Cr dans la proportion de 0,1 à 56 pour cent atomique, Co dans la proportion de 0 à 7 pour cent atomique, Mn dans la proportion de 4,5 à 8,5 pour cent atomique, Al dans la proportion de 0 à 3 pour cent atomique, Fe dans la proportion de 0 à 2,5 pour cent atomique, Mo dans la proportion de 0 à 6,5 pour cent atomique, La dans la proportion de 0 à 30 pour cent atomique, et Mm dans la proportion de 0 à 30 pour cent atomique,

où la proportion totale desdits éléments est égale à 100 pour cent atomique dudit second composant.

32. Electrode négative d'hydrure de métal selon la revendication 26, où ledit second composant comprend un alliage de la composition suivante :

 $\mathrm{V_{18}Ti_{15}Zr_{18}Ni_{29}Cr_{5}Co_{7}Mn_{8}}$ 

33. Pile à stockage électrochimique d'hydrogène comprenant : des particules de poudre composite hétérogène non uniforme destinées à un stockage électrochimique d'hydrogène comprenant :

un premier composant comprenant des matériaux présentant la composition suivante :

 $(Mg_xNi_{1-x})_aM_b$ 

5

15

25

30

35

40

45

50

55

M représente au moins un élément modificateur choisi parmi le groupe constitué de Ni, Co, Mn, Al, Fe, Cu, où. Mo, W, Cr, V, Ti, Zr, Sn, Th, Si, Zn, Li, Cd, Na, Pb, La, Ce, Pr, Nd, Mm, et Ca,

b va de 0 à moins de 30 pour cent atomique, et a + b = 100 pour cent atomique dudit premier matériau de composant, 0,25 ≤ x ≤ 0,75, mélangé à un second composant comprenant au moins un élément choisi parmi le groupe constitué de :

Ti dans la proportion de 0 à 60 pour cent atomique,

Zr dans la proportion de 0 à 40 pour cent atomique, V dans la proportion de 0 à 60 pour cent atomique, Ni dans la proportion de 0 à 57 pour cent atomique, Cr dans la proportion de 0 à 5 pour cent atomique, Cu dans la proportion de 0 à 56 pour cent atomique, Co dans la proportion de 0 à 15 pour cent atomique, Mn dans la proportion de 0 à 20 pour cent atomique, Al dans la proportion de 0 à 20 pour cent atomique, Fe dans la proportion de 0 à 10 pour cent atomique, Mo dans la proportion de 0 à 8 pour cent atomique, La dans la proportion de 0 à 30 pour cent atomique, et Mm dans la proportion de 0 à 30 pour cent atomique,

où la proportion totale desdits éléments est égale à 100 pour cent atomique dudit second composant.

THIS PAGE BLANK (USPTO)